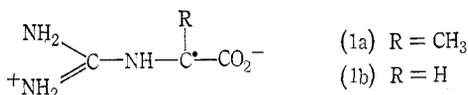


AN E.S.R. STUDY OF IRRADIATED GLYCOCYAMINE

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[Manuscript received September 11, 1970]

The magnitude of the isotropic value of α - and of β -proton hyperfine splitting tensors in organic free radicals reflects, *inter alia*, the distribution of the unpaired electron spin density throughout the framework of the free radical.^{1,2} Previously, we commented on this in regard to the relatively low hyperfine splitting of the methyl protons, 53 MHz, in the free radical, $\text{CH}_3\text{C}(\text{OH})\text{CO}_2^-\text{Li}^+$, trapped in γ -irradiated lithium DL-lactate³ and have since noted that a similar low value, 48 MHz, has been observed for the methyl proton splitting in the free radical (1a), trapped in irradiated *N*-amidino-L(?)alanine.⁴



In this latter free radical, the low value of the hyperfine splitting arises from delocalization of the unpaired electron into the π -electron framework of the guanidino functional group. Bearing this delocalization in mind, we hoped to be able to resolve and subsequently correlate the elements of the α -proton- and the ^{14}N -hyperfine splitting tensors in the free radical (1b), which we expected to be trapped in γ -irradiated single crystals of glycocyamine (guanidinoacetic acid).

Our e.s.r. measurements at room temperature confirmed that the free radical trapped in the crystal had the expected structure (1b), but we were able to resolve only the α -proton hyperfine splittings, which gave an isotropic value of 51.8 MHz (18.5×10^{-4} T). We were unable to resolve any hyperfine structure due to ^{14}N interactions, though the magnitude of the α -proton hyperfine splittings and the very broad lines in the spectra from irradiated crystals grown from H_2O and from D_2O (see below) indicated that there was significant unpaired electron density in the guanidino group.

The crystals were irradiated to a dose of 2–4 Mrad with ^{60}Co γ -rays at room temperature and the e.s.r. spectra were obtained as before.³ As the crystal structure of glycocyamine was unknown, three orthogonal reference axes (x , y , z) were chosen

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¹ Fischer, H., *Z. Naturf. (A)*, 1965, **20**, 428.

² Fischer, H., *Z. Naturf. (A)*, 1964, **19**, 866.

³ Whelan, D. J., *Aust. J. Chem.*, 1970, **23**, 37.

⁴ Drews, R. E., and Rowlands, J. R., *J. chem. Soc. (B)*, 1966, 297.

with reference to the external crystal morphology—the y -axis corresponding to the long axis of the crystal, the x -axis being parallel to the broader face in the plane perpendicular to the y -axis.

TABLE 1
HYPERFINE PARAMETERS (MHz) FOR THE α -PROTON IN THE FREE RADICAL (1b) FROM IRRADIATED GLYCOCYAMINE

$$A_{\text{iso}}(\alpha\text{-H}) = -51.8 \text{ MHz}; g_{\text{iso}} = 2.0034$$

Tensor in Relation to xyz Axes	Principal Values	Direction Cosines
(-)	38.3 11.1 13.2	-75.2 (0.382, ± 0.857 , 0.346)
	68.3 4.8	-51.9 (-0.371, ± 0.485 , -0.792)
	48.7	-28.2 (-0.846, ± 0.174 , 0.503)

TABLE 2
E.S.R. PARAMETERS FOR FREE RADICALS $R^1R^2C\dot{C}H$ RELATED TO (1)
 α refers to $A_{\text{iso}}(\alpha\text{-H})$, β refers to $A_{\text{iso}}(\beta\text{-CH}_2)$; units in MHz

Radical	Host	g -Value	$A_{\text{iso}}(\text{H})$	Ref.
$\text{COC}\cdot\text{HNHCOC}\cdot\text{NH}$	diketopiperazine	—	46(α)	a
$\text{CH}_3\text{CONHC}\cdot\text{HCO}_2\text{H}$	<i>N</i> -acetyl glycine	2.0033	50(α)	b,c
$+\text{NH}_3\text{CH}_2\text{CONHC}\cdot\text{HCO}_2^-$	glycylglycine	2.0032	51(α)	d
$+\text{NH}_2=\text{C}(\text{NH}_2)\text{NHC}\cdot\text{HCO}_2^-$	glycocyamine	2.0034	52(α)	e
$+\text{NH}_3\text{CH}_2\text{CONHC}\cdot\text{HCO}_2\text{H}$	glycylglycine hydrochloride	—	53(α)	f
$\text{NH}_2\text{CONHC}\cdot\text{HCO}_2\text{H}$	<i>N</i> -carbamylglycine	2.0033	55(α)	g
$+\text{NH}_3\text{C}\cdot\text{HCO}_2^-$	glycine	2.0036	62(α)	i
$\text{CH}_3\text{C}\cdot\text{HCO}_2^-$	<i>L</i> -alanine	—	61(α) 70(β)	j
$\text{CH}_3\text{C}\cdot\text{HCONH}_2$	propionamide	2.0032	64(α) 67(β)	k
$\text{CH}_3\text{CONHC}\cdot(\text{CH}_3)\text{CO}_2\text{H}$	<i>N</i> -acetylalanine	—	55(β)	l
$+\text{NH}_2=\text{C}(\text{NH}_2)\text{NHC}\cdot(\text{CH}_3)\text{CO}_2^-$	<i>N</i> -amidoalanine	—	48(β)	m

^a Lin, W. C., and McDowell, C. A., *Can. J. Chem.*, 1963, **41**, 9; *J. chem. Phys.*, 1963, **39**, 848. ^b Mangiaracina, R. S., *Radiat. Res.*, 1967, **32**, 27. ^c Miyagawa, J., Kurita, G., and Gordy, W., *J. chem. Phys.*, 1960, **33**, 1599. ^d Lin, W. C., and McDowell, C. A., *Molec. Phys.*, 1961, **4**, 333. ^e This work. ^f Box, H. C., Freund, H. G., and Lilga, K. T., *J. chem. Phys.*, 1963, **38**, 2100. ^g Rao, D. V., and Katayama, M., *J. chem. Phys.*, 1962, **37**, 382. ^h Box, H. C., Freund, H. G., and Budzinski, E. E., *J. Am. chem. Soc.*, 1966, **88**, 658. ⁱ Collins, M. A., and Whiffen, D. H., *Molec. Phys.*, 1966, **10**, 317. ^j Horsfield, A., Morton, J., and Whiffen, D. H., *Molec. Phys.*, 1961, **4**, 425. ^k Hamrick, P. J., Shields, H. W., and Parkey, S. H., *J. Am. chem. Soc.*, 1968, **90**, 5371. ^l Katayama, M., *J. molec. Spectrosc.*, 1962, **9**, 429. ^m Ref. 4.

When the magnetic field was parallel to each of these three axes, the e.s.r. spectra consisted of two well-defined but relatively broad lines of equal intensity. The width of each line in these spectra from crystals grown from H_2O was $(9.0 \pm 0.5) \times 10^{-4}$ T, while that from crystals grown from D_2O was $(8.0 \pm 0.3) \times 10^{-4}$ T. These line-widths are much broader than those usually observed ($3\text{--}6 \times 10^{-4}$ T) from

simple radicals in oriented single crystals, e.g. $(\text{CH}_3)_2\text{CCO}_2\text{H}$ in α -aminoisobutyric acid or $\text{CH}_3\text{CHCONH}_2$ in propionamide.

On rotation about each of the three axes, the spectra, which were relatively isotropic with respect to $g = 2.0034$ along all three axes, showed an anisotropy in their hyperfine splitting characteristic of the interaction of the unpaired electron with an α -proton. The site-splittings observed in the spectra were consistent with those from a free radical trapped in a monoclinic host—the y -axis of our crystals corresponding to the b -axis of a monoclinic (a^*bc) or (abc^*) host.⁵ A full description of the spectra is given in Table 1.

Table 2 summarizes the α -proton hyperfine splittings and g -values for various free radicals related to (1a) and (1b). In all of these free radicals, g_{iso} is approximately 2.0032 (± 0.0002), which is typical of that for π -electron radicals, and the magnitude of $A_{\text{iso}}(\alpha\text{-H})$ is significantly lower than that usually observed (60 MHz) in related free radicals in which delocalization onto X in $\text{XCH}\cdot\text{CO}_2\text{H}$ is not favoured,⁵ in the ground state. However, we would point out that it is unusual for the hyperfine splitting of the β -proton interaction in (1a) to be less than that for the α -proton in (1b).^{1,2,5}

Acknowledgments

The irradiations were carried out at Central Research Laboratories, ICIANZ Ltd, through the courtesy of Drs H. A. J. Battaerd and P. G. S. Shah. The tensor in Table 1 was diagonalized by a program provided by Dr D. J. Elias of our laboratories.

⁵ Morton, J. R., *Chem. Rev.*, 1964, **64**, 453.