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G. Lassmann ^{a b} & W. Damerau ^{a b}

 ^a Institute of Biophysics, German Academy of Sciences, Berlin
 ^b Physico-Chemical Centre, Research Centre of Molecular Biology and Medicine, German Academy of Sciences, 1115, Berlin-Buch, Lindenberger Weg 70
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Electron spin resonance of radicals in X-irradiated single crystals of N-substituted amino acids II. Sarcosine. HCl

by G. LASSMANN and W. DAMERAU Institute of Biophysics, German Academy of Sciences, Berlin⁺

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1. INTRODUCTION

In the course of investigations of N-substituted amino acids in the previous note [1] radicals with uncharged amino groups in N-benzoylalanine have been reported. The present work is concerned with a radical in sarcosine. HCl crystals containing a charged amino group. Two types of radical are formed in sarcosine. HCl [2] and principal values of g and hyperfine tensors are given in the present paper. In addition to these radicals, on low temperature irradiation an additional V_K centre (Cl₂⁻) has been detected in sarcosine. HCl [3].



Figure 1. Top and side view of a crystal of sarcosine. HCl with abc' axes.

2. EXPERIMENTAL

Sarcosine. HCl is monoclinic with the unit cell constants

$$a_0 = 4.42 \text{ Å},$$

 $b_0 = 5.94 \text{ Å},$
 $c_0 = 8.81 \text{ Å},$
 $\beta = 117^{\circ} \ddagger.$

[†] Present address: Physico-Chemical Centre, Research Centre of Molecular Biology and Medicine, German Academy of Sciences, 1115 Berlin-Buch, Lindenberger Weg 70.

‡ For the crystal data we are indebted to Dr. Niebsch from the Institute of Mineralogy, Humboldt University, Berlin. The crystals were grown from aqueous HCl solution by slow evaporation. Crystals deuterated in exchangeable positions were prepared from D_2O/DCl solutions. Figure 1 shows a sarcosine. HCl crystal with the *abc'* axes used (dimensions: $7 \times 1 \times 1$ mm). Experimental conditions for X-irradiation and E.S.R. measurements were as in [1].

3. Results

After room temperature irradiation of sarcosine. HCl

$$(HOOC-CH_2-NH_2-CH_3.Cl^{(-)})$$

two different overlapping E.S.R. spectra occur (figure 2 *a*). Four lines with equal intensities indicated by bars belong to type I. If the crystal is annealed up to +120 °C type I is destroyed and the second type of radical remains (figure 2 *b*). The corresponding hyperfine structure represents a doubled 1:2:1 triplet with a 1:1:1 triplet substructure. From the plots for anisotropic variation of *g* factor and hyperfine splittings the principal values of both types of radical have been



Figure 2. E.S.R. spectra of a single crystal of sarcosine. HCl after X-irradiation at room temperature. (a) before annealing (type I), (b) after annealing up to 120°C (type II). If not otherwise stated field increases from left to right.

evaluated and are summarized in table 1. The E.S.R. spectra of type I in the deuterated crystal are the same as in the undeuterated crystal, whereas for type II quite different spectra occur (figure 3).

4. DISCUSSION

4.1. Identification of radicals

The two doublet splittings of type I give typical isotropic and anisotropic hyperfine couplings (table 1) due to two α protons [4]. Type I must therefore be HOOC-CH₂, which is observed also in malonic acid [5] and glycine [6]. Within experimental error the two α protons are equivalent. From direction cosine results, the axis of the π orbital is parallel to the monoclinic *b* axis of the crystal and

	Tensor	Principal values	Isotropic	Anisotropic	Remarks	9 8	irection cosines b	۵
	od	2 ·0050 2 ·0029 2 ·0040	2.0040		⊥ to radical plane	$\begin{array}{c} 0.98 \\ -0.17 \\ -0.10 \end{array}$	-0.15 -0.97 0.18	0.12 0.16 0.98
Type I	H_{α_1}	- 31 • 5 - 21 • 0 - 13 • 7	- 22		⊥ to radical plane ∥ to CH1-bond	0 · 90 0 - 0 · 43	$\begin{array}{c} -0.04\\ 1\\ 0.02\end{array}$	$\begin{array}{c} 0.43\\ 0\\ 0\\ 0.90\end{array}$
	${ m H}_{lpha_2}$	-9.7 -21.0 -32.6	- 21	+11.4 +0.1 -11.5	to CH ² -bond to radical plane	0 · 0 · 0 0 · 0 - 08	- 0 • 06 0 • 99 0 • 03	-0.08 0.02 -0.99
	ø	2 ·0033 2 ·0019 2 ·0057	2 · 0036		L to radical plane	0.95 0.07 -0.31	90·0 - 0-00 -	$\begin{array}{c c} 0 \cdot 32 \\ - 0 \cdot 04 \\ 0 \cdot 95 \end{array}$
Type II	H_{α}	- 35 ·9 - 23 ·0 - 11 ·0	- 23 · 3	-12.6 +0.3 +12.3	L to radical plane to CH-bond	-0.93 0.04 0.38	0 · 11 0 · 98 0 · 15	0.37 - 0.18 - 0.31 0.31
	$2H_N$	26.7 22.7 20.6	+23.3	+3.4 -0.6 -2.7		0.83 0 0.56	0 - 0	0 · 56 0 - 0 · 83
	$\mathbf{N}_{\mathbf{\alpha}}$	- 3 · 4 - 1 · 1 - 3 · 9	-2.8	-0.6 +1.7 -1.1		-0.84 0.16 0.53	$\begin{array}{c} 0 \cdot 07 \\ 0 \cdot 98 \\ - 0 \cdot 18 \end{array}$	$0.55 \\ 0.12 \\ 0.83$
Table 1. P	rincipal values a	and direction cos	sines for HOOC-	ĊH2 (type I) and splittings in gauss	HOOC-ĊH-ŇH2-CH3).	(type II) in s	arcosine.HCl (h	lyperfine

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Figure 3. E.S.R. spectra of a sarcosine. DCl crystal after irradiation at room temperature and annealing up to 120°C.

the calculated angle between the two CH bonds is $121^{\circ} \pm 5^{\circ}$. Using Fischer's semi-empirical formula [7], with $\Delta(\text{COOH}) = 0.072$, a spin density of $\rho_{\rm C} = 0.928$ is obtained.

In the second type of radical one α proton, one nitrogen nucleus and two equivalent β protons with small anisotropy are interacting with the unpaired electron. Principal values are given in table 1. The resulting structure of the type II radical is HOOC-CH-NH₂-CH₃. From the direction cosines for g and α -proton tensors it follows that the orientation of the axis of the π orbital is parallel to the b axis. Consequently the orientations of the radical planes of the two different types of radical in the sarcosine.HCl crystal are the same. A similar result was found for the radicals in N-benzoylalanine [1].

4.2. NH- β protons

The two β -protons are equivalent even at 77K, indicating that the NH protons change their positions faster than 10⁷ Hz at low temperature. The structure of the tensor for NH- β protons is similar to that for CH₃- β protons [8]. The isotropic value is 23.3 gauss and the anisotropy is small (only ≈ 3 gauss). The N tensor with an isotropic value of -2.8 gauss agrees with other hyperfine data for N nuclei [9].

4.3. Spin density in radicals with charged amino groups

For an estimation of the spin density $\rho_{\rm C}$ at the central carbon, isoelectronic radicals with alkyl groups or charged amino groups are considered (table 2). An application of Fischer's formula [7] for a calculation of $\rho_{\rm C}$ is impossible because of the unknown $\Delta(X)$ value for the ($\dot{\rm NH}_2$ -CH₃) group. Therefore in table 2 some isotropic hyperfine splittings are compared for radicals (-)OOC-CH-X. The α -proton splitting increases with increasing spin density at the central carbon and decreasing mesomeric effect of the group X. Generally in isoelectronic radicals the α -proton splitting in radicals with charged amino groups is larger (and β -proton splitting is smaller) than in the corresponding radicals with alkyl groups. Therefore Downloaded by [New York University] at 19:43 06 January 2015

No.	Radical	Compound	aH ^a	aH ^β	an	bc	γX	Remarks	Ref.
+	с́н-сн₃ Н	Ethane (liquid)	22 · 4	26.9		0.92	$\Delta(CH_3) = 0.081$		[11]
3	ĊH-ȟH₃ │ H	Methylammonium alum (crystal)	25	19.2	4.1	> 0 · 92	$\Delta(\dot{\rm h}{\rm H_3})<0\cdot081$		[12]
ñ	ён-сн ₃ соо(-)	Alanine (crystal)	19.5	25.1	Ι	0.85			[13]
4	ĊH-ŇH3 COO(-)	Glycine (crystal)	22.7	17.2	3.1	> 0 • 85			[14]
ĸ	ĊН-СН₂-СН₃ СОО(-)	n-butyric acid (flow)	20.3	24 · 1	I	0.86	$\Delta(CH_2-CH_3) = 0.078$	AX evaluated from (CH ₃) ₂ > Ċ-CH ₂ -CH ₃ (11)	[15]
9	ĊH-ȟH₂–CH₃ COOH	Sarcosine.HCl (crystal)	23.3	23 · 3	2.8	> 0 • 91	$\Delta(\dot{\rm h}{\rm H_2-CH_3}) < 0.024$		This work
٢	ĊH-CH₂−ȟH₃ COO(-)	β -alanine (flow)	21 · 4	24 · 5	$3\cdot 3(\gamma)$	0.91	$\Delta(\mathrm{CH}_{2}-\mathrm{\mathring{C}H}_{3})=0\cdot024$	AX evaluated from (CH ₃) ₂ > Č-CH ₂ -NH ₃ (15)	[15]

Isoelectronic radicals with charged amino groups and alkyl groups (hyperfine splittings in gauss). Table 2.

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the mesomeric effect of a charged amino group must be smaller than in the isoelectronic alkyl group:

$$\Delta(NH_3) < \Delta(CH_3) = 0.081,$$

 $\Delta(NH_2-CH_3) < \Delta(CH_2-CH_3) = 0.078.$

Comparing the α -couplings for radical No. 7 with those from No. 4 and 6 in table 2, the inequality $(NH_2-CH_3) < (NH_3) < 0.024$ is valid and therefore for radical type II $\rho_C > 0.91$. The conclusion can be drawn that the mesomeric effect of charged amino groups is much smaller (<2.4 per cent) than that of uncharged amino groups ($\approx 22-42$ per cent) [1]. This is due to the fact that the lone pair at the nitrogen supports the delocalization of the unpaired π electron into the uncharged amino group, whereas in the charged group with its tetravalent nitrogen this lone pair is bound[†]. The capacity of NH protons for hyperconjugation is less than that of CH protons, as indicated by the smaller β -proton couplings in charged amino groups relative to isoelectronic alkyl groups.

4.4. Deuterium exchange in radical type II

The correct analysis of spectra in figure 3 from annealed deuterated sarcosine. DCl demonstrates a hyperfine interaction with one nitrogen nucleus and three deuterons. The construction of the theoretical spectra for the deuterated crystal using the corresponding three proton splittings from figure 2 (b) divided by the factor 6.5 leads to the lines plotted in figure 3. They are in good agreement with the experimental spectra. In the radical DOOC- $\dot{C}D-\dot{N}D_2-CH_3$ the CH proton is exchanged by deuterium. This exchange cannot take place before irradiation, because in the spectrum after room temperature irradiation the four lines of type I are unchanged in the deuterated crystal. The spectra in figure 3 are found before annealing and the exchange of CH protons can therefore occur only during the conversion of type I into type II. Type I abstracts a proton from an intact lattice molecule giving type II. The process of conversion of the two types of radical and some aspects of the radiation chemistry of amino acids regarding the formation of primary radicals (at 77°K) and their conversion in secondary ones will be published for sarcosine. HCl N-benzoylalanine and leucine elsewhere [16].

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† This rule seems to be valid also in the similar case of phosphorus. In the radical $>\overline{P}-\dot{C}H-OH$

a splitting $a_{\rm H} = 14.8$ gauss has been found but in the charged radical

 $a_{\rm H} = 17.8-18.0$ gauss [10]. A stronger abstraction of spin density from the central carbon by the lone pair at the phosphorus can explain the smaller α -proton splitting in the first case.

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