ESR of Gamma Irradiation Damage Centers in Single Crystals of Thriethanolamine Hydrochloride

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We have observed two radicals in the ESR spectra of γ-irradiated single crystals of thriethanolamine hydrochloride: $R-\dot{N}H$ and $HN=\dot{C}-R$.

Free radicals produced by gamma irradiation in single crystals of thriethanolamine hydrochloride (**1**) have been investigated between 100 and 440 K with ESR. The radicals in **1** were identified as π- and σ-electron radicals. The ESR spectra of the radicals were unchanged and undiminished at room temperature more than three years after irradiation. The spectra of single crystals were taken at 5-degree intervals for the magnetic field H being applied in each of the three crystallographic planes ab, bc, and ca.

A hyperfine splitting pattern of the obtained spectra is shown in Figs. 1 a, b and c at all orientations of the magnetic field. These spectra consist of 12-lines. In the spectra, the outer pair of triplets is due to a σ-electron radical of the type $R-\dot{N}H$. This radical splits into double lines because of the proton, then each line also splits into triplet lines owing to the nitrogen. Our average value of the proton splitting directly attached to the nitrogen is about 85 G, and the nitrogen splitting is approximately 12 G. Our splitting values are in a good agreement with those derived from σ-electron radicals for $CNCH_2CONHCO\dot{N}H$ and $NH_2COCH_2CO\dot{N}H$ [1, 2], where it was found that the average splitting values were 85.7 ∓ 1 G, 81.3 ∓ 0.7 G for proton and 11.6 ∓ 0.5 G, 14.3 ∓ 1 G for nitrogen. We have obtained g_{av} values from the ESR spectra (Table 1). The g_{av} value is exactly the same as the one reported in [1], but slightly different that reported in [2].

The inner pair of triplets in the spectra are due to the π-electron radical of the type $HN=\dot{C}-R$. Similar splittings have been observed in this radical too. Our average values for a_H and a_N are found to be 17 G and 7 G, respectively. While these values have been reported [1] to be $a_H = 19$ G and $a_N = 5$ G for the $NC\dot{C}HCONHCONH_2$ radical, which is consistent with our data. However, we also stress that our $g_{av} = 2.0030$ is the same as the one in [1] and is almost the same as the one in [2].

The angular variations of g of the σ- and π-electron radicals at room temperature with 5-degree increments of the orientation of the magnetic field are shown in Figs. 2 and 3. Both the g and A tensors of all radicals were constructed by taking the second order effects into account. The principal values obtained after diagonalization of the tensors are given in Table 1. The values of g and the hyperfine coupling

Table 1. The ESR parameters of $R-\dot{N}H$ and $HN=\dot{C}-R$ radicals observed in $(HOCH_2CH_2)_3N \cdot HCl$.

Radical	Principal values of A (G) and g		Direction cosines		
$R-\dot{N}H$	a_H	88.0	−0.06	0.040	0.094
		84.0	0.499	0.990	0.040
		83.0	0.901	−0.600	−0.03
	a_N	20	−0.0039	0.0037	0.995
		9	−0.048	0.0994	0.0038
		7	0.996	0.047	0.0037
	g_a =	2.0034	−0.122	0.094	−0.986
	g_b =	2.0022	−0.3636	−0.9664	−0.0366
	g_c =	2.0019	−0.9099	0.3660	0.1555
	g_{av} =	2.0025			
$HN=\dot{C}-R$	a_H	7	−0.266	0.901	−0.0089
		15	−0.289	−0.0089	0.9949
		28	0.903	−0.299	0.00011
	a_N	12	−0.75	−0.036	0.990
		5	−0.990	−0.0043	0.0069
		3	−0.0069	0.991	0.036
	g_a =	2.0036	0.9696	−0.1888	0.0149
	g_b =	2.0034	0.2001	0.9001	−0.1034
	g_c =	2.0020	0.0059	0.1049	0.09696
	g_{av} =	2.0030			

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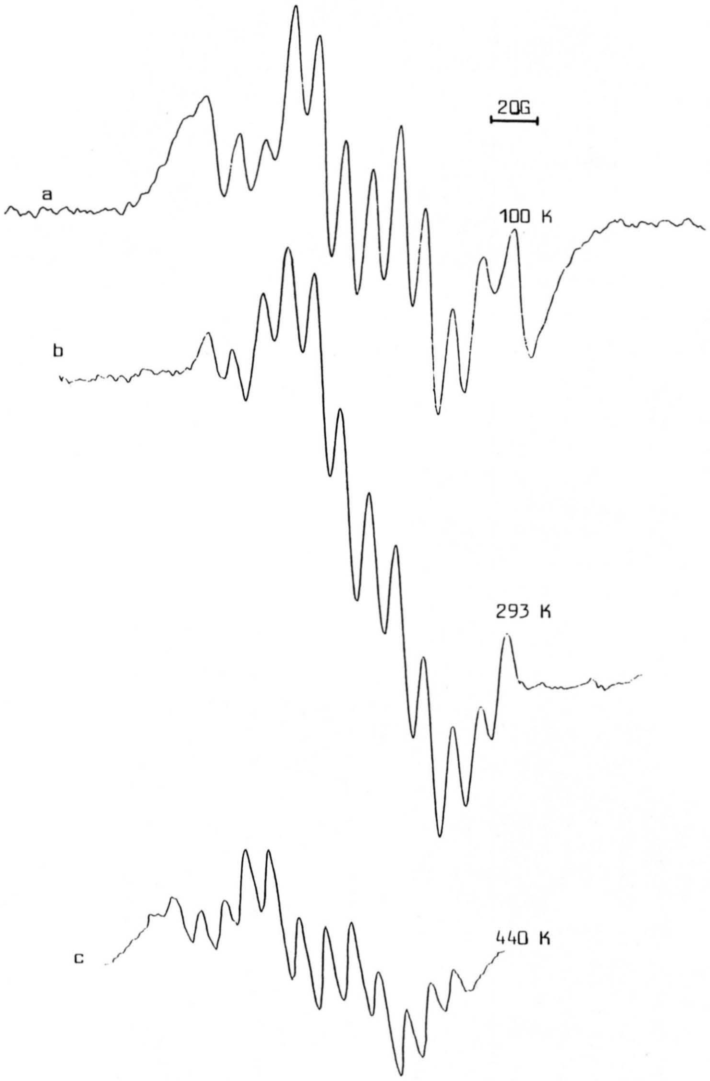

Fig. 1. ESR spectrum of $(HOCH_2CH_2)_3N \cdot HCl$ single crystal at a) 100 K, b) 293 K and c) 440 K when the magnetic field is parallel to the *a*-axis.

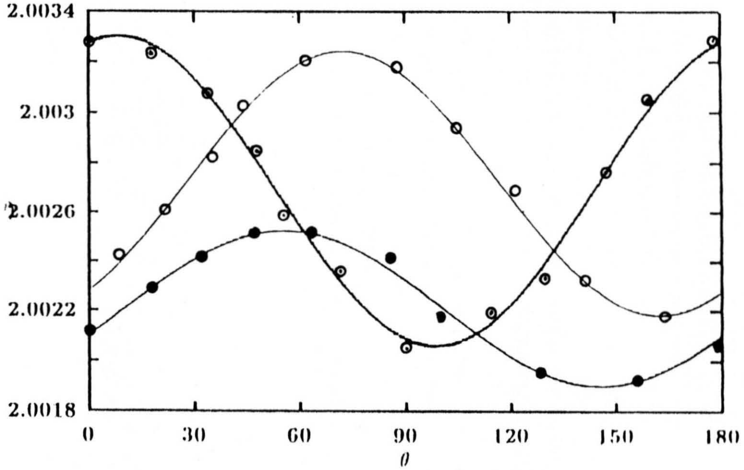

Fig. 2. The angular variations of the *g*-tensor for the *a*- (○), *b*- (●), and *c**- (⊙) axes of the $R-\dot{N}H$ radical.

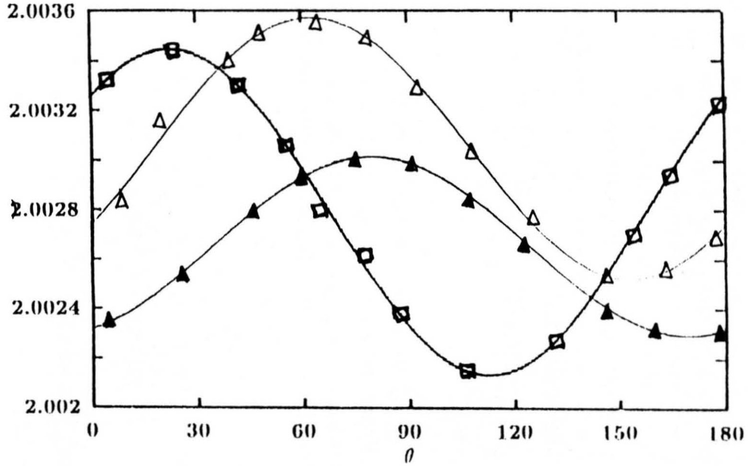

Fig. 3. The angular variations of the *g*-tensor for the *a*- (△), *b* (▲), and *c**- (□) axes of the $HN=\dot{C}-R$ radical.

constants for the σ- and π-radicals did not change appreciably with temperature. Our values of the hyperfine splitting constant of proton and nitrogen for $R-\dot{N}H$ and $NH=\dot{C}-R$ are consistent with [1–8]. Since we do not observe any site splitting we can state that the 2 molecules in the unit cell of the crystal are magnetically equivalent.

Experimental

Single crystals of **1** were grown from an aqueous solution. From the X-ray diffraction studies we have found that the single crystals are orthorhombic with space group $P2_12_12_1$, and its unit cell dimensions are $a = 10.11$, $b = 14.80$, and $c = 8.70$ Å. The unit cell contains 2 molecules. The crystals were irradiated at room temperature by a ^{60}Co γ-ray source of 0.3 Mrad/h for 24 hours. The ESR spectra were recorded with a Variant model E-109C ESR spectrometer using 2 mW microwave power. The low and high temperature measurements from 100 K to 440 K were carried out using a variant temperature controller unit. The crystals were rotated on a Lucite pillar about their crystallographic axes, and the angle of rotations was read on a scale graduated in degrees. The ESR spectra, using several single crystals at several times and also powders of the compound, were reproducible. The g factor was found by comparison with a DPPH sample ($g = 2.0036$).

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