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Electron paramagnetic resonance of gamma-irradiated single crystals of 3-nitroacetanilide

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Abstract

The electron paramagnetic resonance of single crystals of 3-nitroacetanilide has been observed and analyzed for different orientations of the crystal in the magnetic field, after being damaged at 300 K by γ-irradiation. The crystals have been investigated between 123 and 300 K. The spectra were found to be temperature independent. The irradiation of 3-nitroacetanilide by γ-rays produces radicals at the nitrogen atoms in the molecule. The principal values of the hyperfine coupling tensor of the unpaired electron and the principal values of the g-tensor were determined.

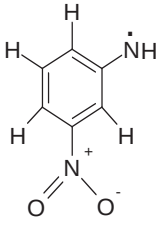
Keywords: EPR; 3-Nitroacetanilide; Radicals; Spin density

1. Introduction

Acetanilide and its derivatives are active components of drugs that show analgesic activity. Analgesics are contained in numerous non-prescription preparations, which relieve pain arising from organic disorders or of psychosomatic origin (Vecchio et al., 2004). Some of the derivatives of acetanilide such as acetoacetanilide, *p*-aminoacetanilide and 3-nitroacetanilide were found to exhibit nonlinear optical properties. It is well known that most of the single crystals of organic materials have been used as scintillators, semiconductors, superconductors, piezoelectrics, thermoelectrics, colour displays, optical memories and so on (Kou and Chen, 1994; Farges, 1994; Ishiguro and Yamaji, 1990; Reynolds, 1963; Babu et al., 2003; Lakshmi et al., 2006). In the present work one of the acetanilide derivatives, 3-nitroacetanilide, single crystals are exposed to high-energy radiation. As a result, the paramagnetic species are generated.

Free radicals are chemical species that possess an unpaired electron in the outer shell of the molecule. Free radicals are formed mainly in case of irradiation of solid. For irradiated solids, they can be generated by homolytic cleavage of a covalent bond, in which a normal molecule fragments into two, each fragment retaining one of the paired electrons. Due to the fact that the unpaired electron is involved in free radicals, these species are paramagnetic and the most used method for detecting free radicals is electron paramagnetic resonance spectroscopy (EPR).

Table 1
Coupling constant in 3-nitroanilino radical

Free radical		Values from simulated spectra (Gauss)	
		Figure	
		1	2
	A_{NH}^{H}	18.17	14.03
	A_{NH}^{N}	13.27	11.98
	$A_{H(2)}$	4.39	4.09
	$A_{H(3)}$	2.85	2.30
	$A_{N(2)}$	4.23	4.13
	$A_{H(4)}$	2.35	1.73

Note: Errors for all the calculated g and A values are estimated as ± 0.0005 and ± 0.5 G, respectively.

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When an unpaired electron in a magnetic field interacts with a nuclear spin, the spectrum splits into two or more lines, which produce a hyperfine structure in the spectrum. The splitting of the spectrum is expressed in terms of a hyperfine coupling constant (A-value in G or mT units), and the relative position of the spectrum is expressed by the spectroscopic splitting factor (g-value, dimensionless). Investigations on the g-tensor and hyperfine coupling constants of the spin carrying nuclei of the species give information about the structure of the species and the structure of the centers (Damian et al., 2005).

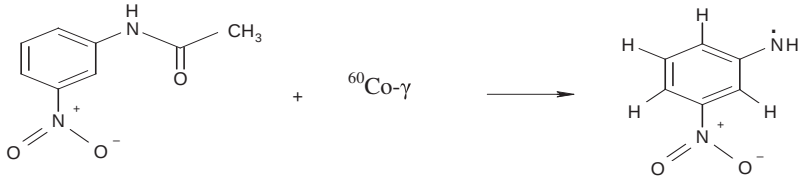
In this paper, we propose the detection of these reactive radicals, which occur after irradiation 3-nitroacetanilide single crystals, by using the EPR method.

2. Experimental details

3-Nitroacetanilide single crystals were grown by slow evaporation of a concentrated aqueous solution. From the X-ray diffraction studies we have found that the single crystal of 3-nitroacetanilide are monoclinic with space group $P2_1$ and their unit cell dimension $a = 9.767$ (2) Å, $b = 13.298$ (3) Å, $c = 13.272$ (3) Å. In the unit cell of 3-nitroacetanilide there are four independent molecules in the asymmetric unit (Mahalakshmi et al., 2002). The single crystals were irradiated at room temperature by a ^{60}Co-γ ray source of 2, 41 kGy/h for 66 h. The spectra were recorded with a Bruker EMX 081 model EPR spectrometer. The low- and high-temperature measurements were carried out between 123 and 300 K using a Bruker control unit. The magnetic field modulation frequency was 100 kHz and the modulation amplitude was 0.5 G. While single crystals were rotated on a Lucite pillar about the crystallographic axes with the help of a commercial computer program and the single crystal, spectra were taken at 5-degree intervals of angels for the magnetic field H being applied in each of the three crystallographic direction xy, yz and zx. Low-temperature measurements were carried out using a Bruker variable temperature control system.

3. Results and discussion

After irradiation of 3-nitroacetanilide by 60Co-γ rays at room temperature, EPR spectra were taken in the temperature range 123–300 K. The spectra were found to be independent of the temperature. However, they were dependent on the orientation of H in the planes which are perpendicular to each other. When investigating the spectra, we observed that owing to H protons, 1:1 doublets intensity ratios occurred, and each of the lines (1:1) splits because of the N-proton and other protons, respectively. As a result, according to the chemical structure of the substance and the available data in the literature (Atherton et al., 1963; Liu et al., 1997; Llyod and Wood, 1971, 1974; Müller et al., 1961; Neugebauer et al., 1975; Scheffler, 1961), these intensity ratios were attributed to the reaction:



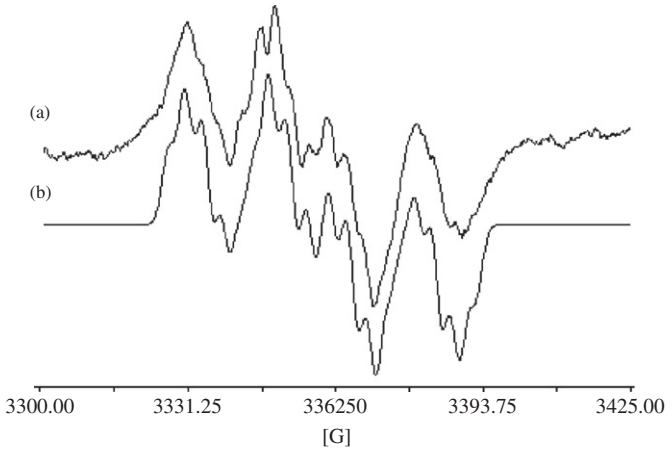


Fig. 1. (a) Upper curves: The EPR spectrum of a γ-irradiated single crystal of 3-nitroacetanilide; the magnetic field is in the xy plane 50° away from x-axis of the crystal. (b) Simulation of the spectrum; the line width is 1.5 G.

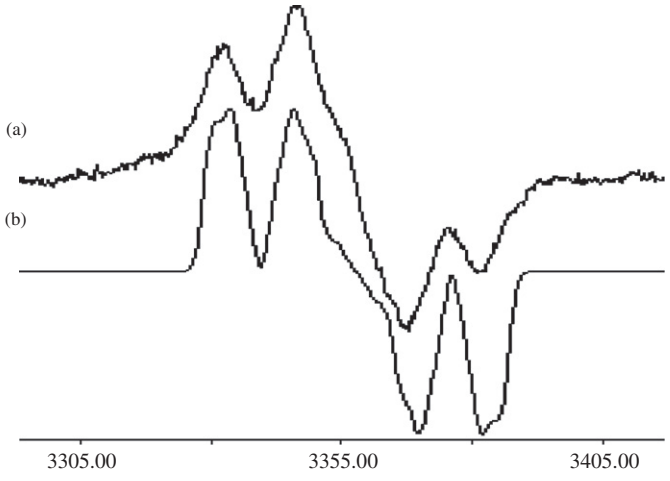


Fig. 2. (a) Upper curves: The EPR spectrum of a γ-irradiated single crystal of 3-nitroacetanilide; the magnetic field is in the yz plane 60° away from y-axis of the crystal. (b) Simulation of the spectrum; the line width is 1.5 G.