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# Electron Spin Resonance Spectra of X-Irradiated Single Crystals of 3, 3′-Dithiodipropionic Acid: “$B\cos^2\theta$” Rule for Sulfur Radicals

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The ESR of X-irradiated single crystals of 3, 3′-dithiodipropionic acid was measured at room temperature. From the analysis of the anisotropy in the spectra, the free radical produced was confirmed to be of the $HO_2C\cdot CH_2\cdot CH_2\cdot S$ form. The principal values of the $g$ factor are 2.003, 2.025, and 2.055, while the isotropic coupling constants for the two $\beta$ protons are 12.4 G and 5.3 G. In this free radical the unpaired electron is mainly concentrated in a 3p$\pi$ orbital of the sulfur atom. For the isotropic coupling constant of the $\beta$ proton in this type of radical, the “$B\cos^2\theta$” rule is applied successfully using the value of 12.8 G for $B$.

Several studies have been made of the electron spin resonance (ESR) of sulfur radicals (R–S) produced by the irradiation of organic disulfides or mercaptans.[1-8] The marked anisotropy in the $g$ factor of sulfur radicals has been explained in terms of a model, in which an unpaired electron is mainly localized in a non-bonding 3p$\pi$ orbital of the sulfur atom. An isotropic coupling constant of a proton in a CH group bonded to the sulfur atom has been assumed as $a=B\cos^2\theta$, where $\theta$ is the dihedral angle between the SCH plane and the CS$\pi$ plane. This equation, with $B=9$G, has been found to be consistent with the observed hyperfine structure of a sulfur radical produced in irradiated L-cystine dihydrochloride.[1] The present work will give another confirmation of the “$\cos^2\theta$” rule.

## Experimental

Single crystals of 3, 3′-dithiodipropionic acid $(HO_2C\cdot CH_2\cdot CH_2\cdot S)_2$ (mp 155—156°C), prepared according to the method of Daneby and Kreuz,[9] were grown by the slow evaporation of a saturated aqueous solution in a refrigerator. The crystal was a thin plate ($3\times 2\times 0.3$ mm$^3$). Since the crystal structure was unknown, a rectangular coordinate system, $a'b'c'$, was defined for the sake of convenience (Fig. 1). The $a'$ axis parallel to the largest edge was selected and the $c'$ axis perpendicular to the largest plane was selected. The interfacial angles were measured with a Model B2 two-circle reflection goniometer from the Stoe and Cie Co. The results are shown in Table 1.

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[3] Y. H. Hahn and R. N. Rexroad, *ibid.*, **38**, 1599 (1963).

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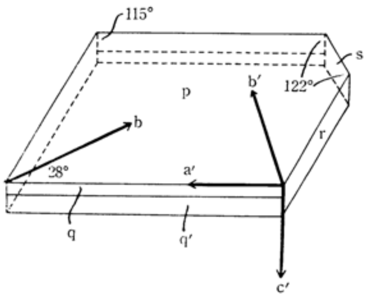

Fig. 1. The crystal form of 3, 3′-dithiodipropionic acid and the coordinate axes employed.

Table 1. Interfacial angles in a crystal of 3, 3′-dithiodipropionic acid

| Plane | Angle (°) | Plane | Angle (°) |
|---|---|---|---|
| *p*, *q* | 109 | *p*, *q′* | 85 |
| *p*, *r* | 85 | *r*, *q′* | 63 |
| *p*, *s* | 103 | *q*, *q′* | 14 |
| *q*, *r* | 63 | *s*, *q′* | 122 |
| *q*, *s* | 124 | *r*, *s* | 61 |

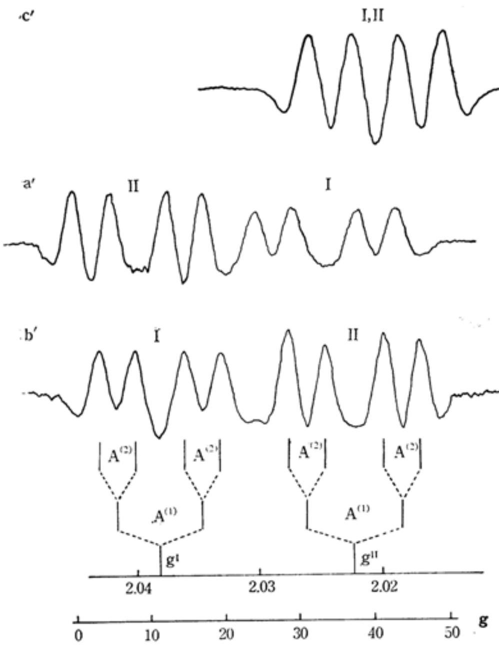

Fig. 2. Second-derivative ESR spectra of an X-irradiated single crystal of 3, 3′-dithiodipropionic acid at room temperature for the magnetic field parallel to the *c′*, *a′*, and *b′* axes.

Single crystals were irradiated wtih X-rays (40 kV, 30 mA) to 1 Mard at room temperature, and then examined with a Varian V-4501 EPR Spectrometer for various orientations of the magnetic field in the *a′b′*, *b′c′*, and *c′a′* planes and in a plane perpendicular to the *b* axis. Typical spectra are shown in Fig. 2.

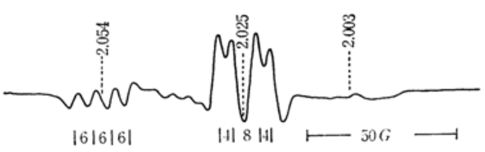

Fig. 3. The second-derivative ESR spectrum for X-irradiated powder of 3, 3′-dithiodipropionic acid.

The spectrum consists of two quartets, which, labeled I and II for the sake of later identification, coalesce to a single quartet for the magnetic field along specified directions. Although the quartet structure is better resolved in the single crystal, it is still evident in the resonance of the irradiated powder shown in Fig. 3. The quartet is nearly isotropic and can arise from two coupling protons with nearly isotropic coupling constants of 8—14 G (av. 12.4 G) and 3—7 G (av. 5.3 G). The *g* factors of the two quartets at 10° intervals in each plane are summarized in Fig. 4. The *g* tensor was obtained by the least-mean-square method based on the relation:

$$g^2 = \boldsymbol{Z}\cdot\mathbf{g}^2\cdot\boldsymbol{Z}, \tag{1}$$

where $\mathbf{g}$ is the *g* tensor, $\boldsymbol{Z}$ is a unit vector along the magnetic field, and *g* is the observed *g* factor for the magnetic field along $\boldsymbol{Z}$. The principal values and principal axes of the *g* tensor are shown in Table 2.

Table 2 shows that the principal values of the *g* factor are the same within the limits of experimental error for the two quartets and that, consequently, the two quartets arise from two different orientations of the same radical species. The three bisectors of the corresponding principal axes ($g^{\rm I}_1$ and $g^{\rm II}_1$, $g^{\rm I}_2$ and $g^{\rm II}_2$, and $g^{\rm I}_3$ and $g^{\rm II}_3$) are found to be parallel within the

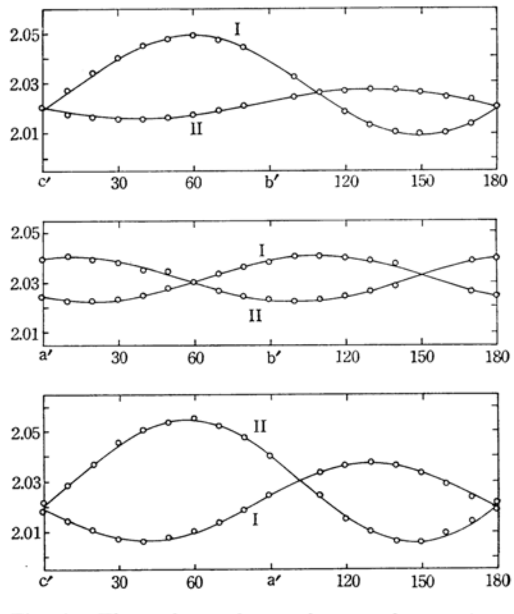

Fig. 4. The observed *g* factors for various orientations of the magnetic field in the *a′b′*, *b′c′*, and *c′a′* planes. The curves are plotted from the data of Table 2 according to Eq. (1).

limits of experimental error. The common bisector, the $b$ axis, lies in the $a'b'$ plane and makes an angle of 28° with the $a'$ axis. When the magnetic field is perpendicular to the $b$ axis, the observed spectrum consists of a single quartet. These facts indicate that the crystal is monoclinic, with the unique axis along the $b$ axis. The direction cosines of the $b$ axis with respect to the $a'b'c'$ system are shown in Table 2.

TABLE 2. PRINCIPAL ELEMENTS OF THE $g$ FACTOR[a)]

| | Principal value | Direction cosines with regard to the $a'b'c'$ system | | |
|---|---|---|---|---|
| $g^{I}_1$ | 2.0032 | 0.488 | −0.324 | 0.811 |
| $g^{I}_2$ | 2.0246 | 0.774 | 0.590 | −0.230 |
| $g^{I}_3$ | 2.0552 | 0.404 | −0.740 | −0.538 |
| $g^{II}_1$ | 2.0037 | 0.520 | −0.327 | −0.789 |
| $g^{II}_2$ | 2.0252 | −0.190 | −0.945 | 0.266 |
| $g^{II}_3$ | 2.0549 | 0.833 | −0.012 | 0.554 |
| $b$ | | 0.846 | −0.533 | 0.000 |

a) The standard deviations are 0.0003 and 1° for the principal values and the directions of the principal axes, respectively.

## Discussion

The principal values of the $g$ tensor observed in 3, 3'-dithiodipropionic acid are almost identical to those of $HO_2C{\cdot}CH(NH_2){\cdot}CH_2{\cdot}S$ (2.003, 2.025, 2.053)[1,4] or $HO_2C{\cdot}CH_2{\cdot}CH(CO_2H){\cdot}S$ (2.003, 2.026, 2.054).[3] The radical responsible for the spectra observed here is apparently $HO_2C{\cdot}CH_2{\cdot}CH^{(1)}H^{(2)}{\cdot}S$, in which an unpaired electron is mainly concentrated in a nonbonding $3p\pi$ orbital of the sulfur atom.

The isotropic (Fermi) coupling constants of the $\beta$ protons $H^{(1)}$ and $H^{(2)}$ can be approximated by the relation[1,10]:

$$\begin{aligned} a_1 &= B\cos^2\theta_1 \\ a_2 &= B\cos^2\theta_2 \\ |\theta_1-\theta_2| &= 120° \end{aligned} \tag{2}$$

where $\theta_i$ is the dihedral angle between the $CS\pi$ plane and the $SCH_i$ plane, and where $B$ is an empirical constant. With the observed values of 12.4G for $a_1$ and 5.3G for $a_2$, Eq. (2) is solved to give:

$$\theta_1 = -53°,\quad \theta_2 = 67°,\ B = 34.7\text{G} \tag{3}$$

or:

$$\theta_1 = 10°,\quad \theta_2 = 130°,\quad B = 12.8\text{G}. \tag{4}$$

For the $HO_2C{\cdot}CH(NH_2){\cdot}CH_2{\cdot}S$ radical,[1,4] the $\beta$ proton coupling constants have been reported as $a_1=9$—10.5G and $a_2\approx0$G. Therefore, $\theta_1\approx-30°$, $\theta_2\approx90°$, and then:

$$a_1 \approx 0.75\,B. \tag{5}$$

The substitution of (3) for $B$ in (5) gives a value of 26 G for $a_1$, which is entirely different from the observed value. Equation (4), however, gives for $a_1$ a value of 9.6 G, which is in good agreement with the observed value.*

It may be concluded that the orientation of the sulfur $3p\pi$ orbital with respect to the $\beta$ methylene group is different in the two sulfur radicals. This conclusion supports the suggestion[1] that the orientation of an odd electron orbital is determined by the crystalline field around the sulfur atom as well as by the hydrogen bonding to it. It seems unlikely that hyperconjugation between the methylene group and the sulfur $3p\pi$ orbital determines their relative orientation.

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* The value of 12.8 G for $B$ cannot be applied to sulfur radicals[4−8] which have been reported to have $g$ tensors different from those of the above-mentioned radicals.