

identification of the dimethylbenzimidazole- $B_{12}$  coenzyme in propionic acid bacteria and rabbit liver suggests that these compounds may be active in a wide range of organisms. In the two bacteria and in rabbit liver, the only biological materials so far examined, a considerable fraction of the total cobalamin is present in the coenzyme forms. These coenzymes may be the main forms of  $B_{12}$  and  $B_{12}$ -like compounds that are catalytically active in the enzymatic reactions of living cells.

The discovery of the coenzyme forms of vitamin  $B_{12}$  opens new possibilities for the study of enzymatic processes, such as the synthesis of methionine,<sup>7</sup> of protein,<sup>8</sup> and of deoxyribonucleosides<sup>9</sup> in which the vitamin is believed to participate. Also, in the treatment of pernicious anemia, the coenzyme theoretically could be more effective than the vitamin under some circumstances. For example, the coenzyme may be absorbed from the digestive tract more readily than the vitamin in the absence of intrinsic factor.<sup>10</sup> Also, conditions may exist in which, because of a block in the conversion of vitamin to coenzyme, only the latter has therapeutic value. These possibilities still require exploration.

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## ELECTRON MAGNETIC RESONANCE OF $CH(COOH)_2$ \*

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We have carried out a detailed analysis of the electron magnetic resonance spectra of single crystals of malonic acid that were subjected to 50-kv. X-ray damage at room temperature. A typical spectrum of an aged single crystal is shown in Figure 1. The positions and intensities of the principal signals (1-4 in Fig. 1) depend on the crystal orientation relative to the applied magnetic field (3,400 gauss). All of the observed spectra can be accounted for in terms of the following set of assumptions.

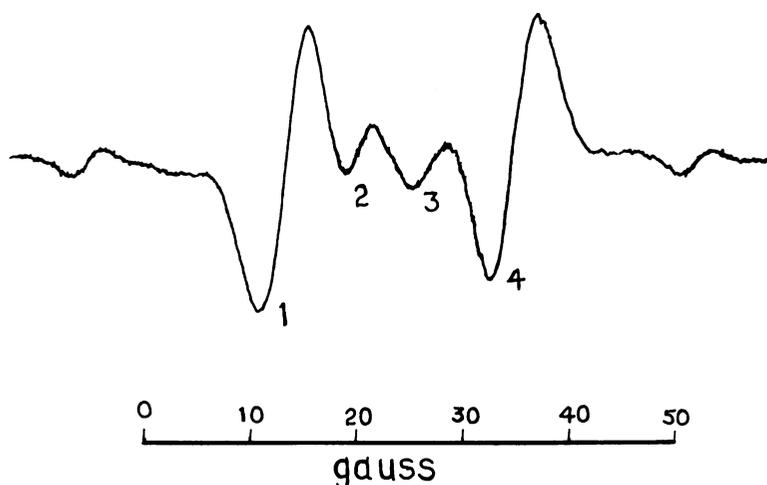


FIG. 1.—Electron magnetic resonance of an X-ray irradiated single crystal of malonic acid. Signals 1, 2, 3, and 4 arise from hyperfine interactions between the odd electron and the  $\alpha$ -proton in the radical  $\text{CH}(\text{COOH})_2$ .

(a) The radicals giving signals 1–4 in Figure 1 have the formula  $\text{CH}(\text{COOH})_2$ .

(b) The carbon, oxygen, and carboxyl hydrogen atoms have very nearly the same positions in the unit cell as they did in the parent  $\text{CH}_2(\text{COOH})_2$  molecules.<sup>1</sup> In  $\text{CH}(\text{COOH})_2$  the  $\alpha$ -proton is coplanar with the three carbon atoms. (Since the two  $\text{CH}_2(\text{COOH})_2$  molecules that are present in the undamaged unit cell of this triclinic crystal are related to one another by a center of symmetry, the above assumptions require that all radicals either have identical orientations, or be related by a center of symmetry. Thus, all  $\text{CH}(\text{COOH})_2$  radicals must give identical spectra for each crystal orientation, as observed.)

(c) The Hamiltonian for the  $\alpha$ -proton-electron hyperfine interaction is,

$$\mathcal{H} = AS_zI_z + BS_xI_x + CS_yI_y \quad (1)$$

where the  $x, y, z$  axes are fixed in the radical, as shown in Figure 2. The observed values of  $A, B, C$  are

$$\begin{cases} |A_{\text{obs}}| &= 30 \pm 2 \text{ Mc} \\ |B_{\text{obs}}| &= 61.5 \pm 2 \text{ Mc} \\ |C_{\text{obs}}| &= 92.5 \pm 2 \text{ Mc} \end{cases}$$

The signs of the above coupling constants were not determined, *but their relative signs were all shown to be the same*. This analysis will be presented in detail elsewhere.

(d) The very weak satellite lines in Figure 1 are due to a second radical species present in relatively lower concentration.

The above experimental values of  $A, B,$  and  $C$  can be understood as follows. Write  $A = a + A_a, B = a + B_a, C = a + C_a$  where  $a$  is the isotropic contact contribution to the hyperfine coupling, and  $A_a, B_a$  and  $C_a$  are the distributed dipolar contributions. Since  $A_a + B_a + C_a = 0$ , the experimental absolute value for  $a$  is

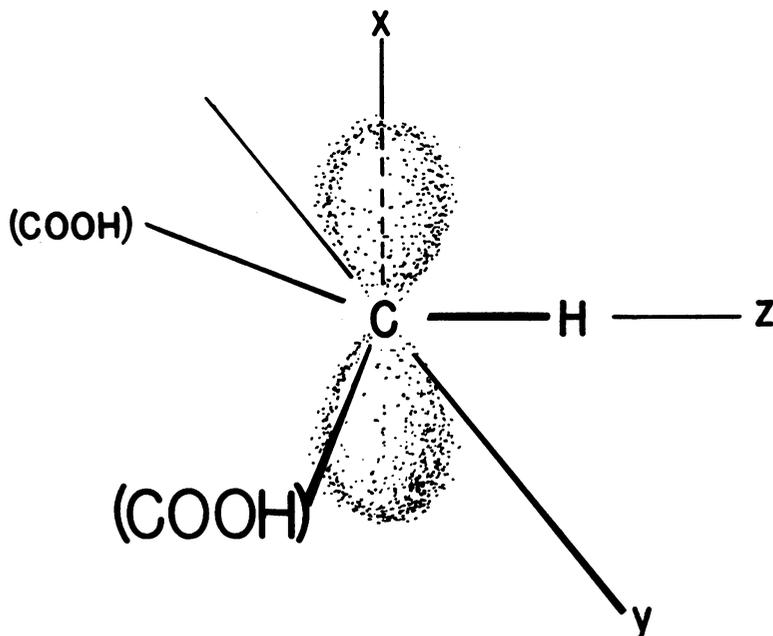


FIG. 2.—Sketch of the  $\pi$ -electron radical  $\text{CH}(\text{COOH})_2$ . The dotted area represents the  $\pi$ -electron spin distribution.

$$\begin{aligned}
 |a_{\text{obs}}| &= \frac{1}{3} |A_{\text{obs}} + B_{\text{obs}} + C_{\text{obs}}| \\
 &= \frac{1}{3} |A_{\text{obs}}| + \frac{1}{3} |B_{\text{obs}}| + \frac{1}{3} |C_{\text{obs}}| \\
 &= 63 \pm 2 Mc
 \end{aligned}$$

This result strongly suggests that  $\text{CH}(\text{COOH})_2$  may be regarded as a  $\pi$ -electron radical with a central carbon atom spin density<sup>2</sup>  $\rho$  of approximately one. That is, for  $\pi$ -electron radicals it has been proposed,<sup>3</sup> and shown on theoretical<sup>4</sup> and experimental grounds,<sup>5</sup> that the isotropic proton hyperfine coupling can be related to the  $\pi$ -electron carbon atom spin density through the equation,  $a = Q\rho$ , where the semiempirical absolute value of  $Q$  is  $63 Mc$ . It has been suggested on theoretical grounds<sup>4, 6</sup> that  $Q$  has a negative sign. If we then take  $a = -63 Mc$ , and use values for  $A_a$ ,  $B_a$ , and  $C_a$  obtained for a single unpaired  $\pi$ -electron in a Slater atomic orbital<sup>7</sup> ( $A_a = 43 Mc$ ,  $B_a = -4.6 Mc$ ,  $C_a = -38.7 Mc$ ), then we obtain the following theoretical values for  $A$ ,  $B$ ,  $C$ .

$$\begin{aligned}
 A_{\text{theo}} &= -20 Mc \\
 B_{\text{theo}} &= -67.6 Mc \\
 C_{\text{theo}} &= -101.7 Mc
 \end{aligned}$$

These theoretical results are in remarkably good agreement with the observed  $A$ ,  $B$ ,  $C$ .<sup>7</sup> On the other hand, a positive sign for  $Q$  leads to complete qualitative as well as quantitative disagreement between the calculated and observed values of  $A$ ,  $B$ ,  $C$ . We therefore believe that our observed values for  $A$ ,  $B$ ,  $C$ , *together with the distributed dipole calculation*,<sup>7</sup> provide strong evidence for a negative value for  $Q$ , and for negative spin densities at  $\sigma$ -protons adjacent to carbon atoms with positive  $\pi$ -electron spin densities.

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<sup>1</sup> The crystal structure of malonic acid has been determined by Goedkoop, J. A., and C. H. MacGillavry, *Acta. Cryst.*, **10**, 125 (1957).

<sup>2</sup> For a discussion of  $\pi$ -electron spin densities in  $\pi$ -electron radicals, see McConnell, H. M., *J. Chem. Phys.*, **28**, 1188 (1958).

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<sup>6</sup> McConnell, H. M., *J. Chem. Phys.*, **24**, 764 (1956). A number of other theoretical studies of ( $\pi$ -electron)-( $\sigma$ -proton) hyperfine interactions have been made, but apparently without explicit evaluation of the sign of the isotropic coupling: See, for example, Bersohn, R., *J. Chem. Phys.*, **24**, 1066 (1956); Weissman, S. I., *J. Chem. Phys.*, **25**, 890 (1956); Jarrett, H. S., *J. Chem. Phys.*, **25**, 1289 (1956); Karplus, M., *J. Chem. Phys.*, **30**, 15 (1959).

<sup>7</sup> McConnell, H. M., and J. Strathdee, *J. Molecular Physics* (in press). In this work an effort was also made to estimate the  $\sigma$ -electron contribution to  $A_d$ ,  $B_d$ ,  $C_d$ . This estimated  $\sigma$ -contribution tends to reduce  $A_{\text{theo}}$  above, but does not substantially affect the present discussion, or conclusions.

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## HIGH-ACCURACY MECHANICAL INTEGRATION BY SHEAR IN VISCOUS LIQUIDS

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*Abstract.*—Integration from the standpoint of instrumentation is provided by any device wherein the time rate of change of an output quantity is accurately proportional to the input quantity. Viscous shear in fluids is a very useful means of realizing integration when mechanical torque acts as the input and the angular velocity of a rotor with respect to a stator is the output. This type of integration is widely used in situations requiring high accuracy for oscillatory inputs with output angles restricted to small magnitudes. The paper outlines the background of viscous-shear integration and develops concepts for describing integrator operation. These concepts are applied to the practically important case of the single-degree-of-freedom integrating gyro unit as an illustration of viscous-shear-integrator operation. The physical dimensions and fluid properties associated with gyro unit integrating components are taken as typical of the problems that may be solved by viscous-shear integrators.

The essential problem is that of causing shearing forces in a thin fluid layer between a cylindrical rotor and a cylindrical stator to produce a torque on the rotor with its magnitude closely proportional to the relative angular velocity between the two cylinders. For practical applications, this proportionality should