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Electron Spin Resonance Study of X-Irradiated Single Crystals of Di-*n*-butyl Oxalate-Urea and Di-*n*-butyl Malonate-Urea Inclusion Compounds*

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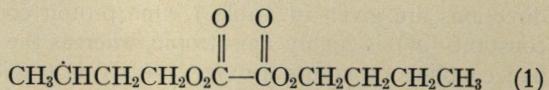
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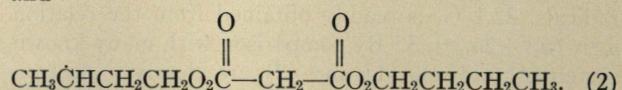
Urea inclusion compounds have been used in numerous x-irradiation studies of aliphatic esters.¹⁻⁴ Single crystals are easily prepared for ESR experiments, and the hexagonal urea matrix provides a common environment for the various guest molecules. To date all published work on saturated and unsaturated ester-urea inclusion compounds indicates that the x-ray produced stable free radicals occur near the carboxyl end of the fatty acid residue. In saturated ester molecules, the observed radicals simply correspond to removal of one hydrogen atom from the carbon atom adjacent to the carboxyl group.^{1,2} Thus, the radicals observed in saturated esters are essentially the same as the well-known radicals⁵ derived from the carboxylic acids. The purpose of this note is to point out that in aliphatic esters the dominant radicals are *not* always produced adjacent to the carboxyl groups. As examples, we discuss below the free radicals observed in urea inclusion crystals of di-*n*-butyl oxalate and di-*n*-butyl malonate.

General experimental details concerning crystal growth, x-irradiation, and ESR measurements may be found elsewhere.⁴ All chemicals used were reagent grade. The crystals were x-irradiated at 77°K and ESR spectra were recorded on a Varian E-3 X-band ESR spectrometer. The spectral simulations were performed

on a Varian 620/i computer. The results are summarized in Fig. 1. Spectra (a) and (b) are the first derivative ESR spectra recorded with the magnetic field along the needle axis (*z* axis) of a di-*n*-butyl oxalate-urea crystal [Fig. 1(a)] and a di-*n*-butyl malonate-urea crystal [Fig. 1(b)]. The proton hyperfine patterns of these two radicals are clearly the same and the computer simulation [Fig. 1(c)] is in good agreement with the experimental results. We conclude that the long-lived radicals produced by x irradiation of di-*n*-butyl oxalate-urea and di-*n*-butyl malonate-urea crystals are, respectively,



and



The spectra are anisotropic except in the crystalline *xy* plane (the plane perpendicular to the needle axis). This behavior is characteristic of urea inclusion compounds and results from rapid motion of the long-chain guest molecules in the tubular cavities of the hexagonal urea matrix.¹ The structure can be thought of as an

TABLE I. Proton coupling constants and *g* values.^{a,b}

Di- <i>n</i> -butyl oxalate radical (1)		Di- <i>n</i> -butyl malonate radical (2)	
(1) $a_z^\alpha = 32.7$	(1) $a_{xy}^\alpha = 17.0$	(1) $a_z^\alpha = 32.8$	(1) $a_{xy}^\alpha = 16.8$
(4) $a_z^\beta = 26.6$	(4) $a_{xy}^\beta = 25.3$	(4) $a_z^\beta = 26.7$	(4) $a_{xy}^\beta = 25.5$
(1) $a_z^\beta = 23.0$	(1) $a_{xy}^\beta = 22.1$	(1) $a_z^\beta = 23.0$	(1) $a_{xy}^\beta = 22.1$
$g_z = 2.0028$	$g_{xy} = 2.0025$	$g_z = 2.0029$	$g_{xy} = 2.0026$

* All a_{xy} and a_z values are believed accurate to within ± 0.3 and ± 1.5 G, respectively. The uncertainty in the *g*-value measurements is ± 0.0002 .

† The numbers in parentheses are the total number of protons with a given coupling constant.

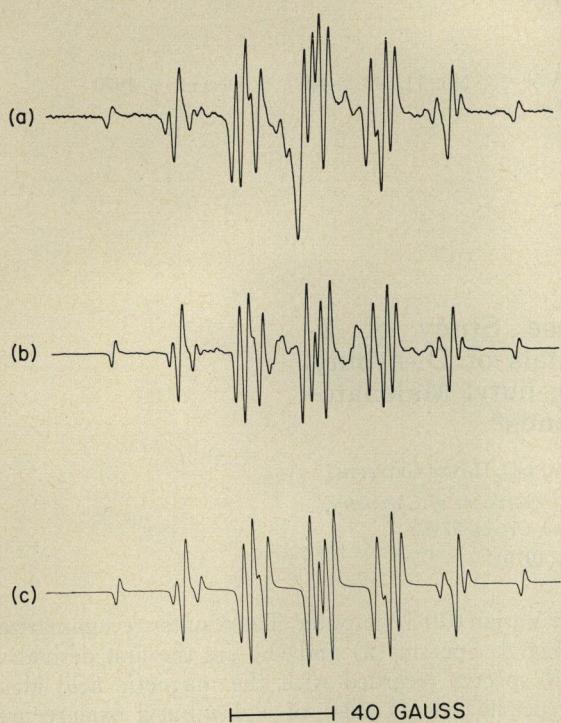


Fig. 1. ESR spectra of x-irradiated single crystals of (a) di-*n*-butyl oxalate at 263°K and (b) di-*n*-butyl malonate at 298°K. In both (a) and (b) the magnetic field is parallel to the *z* axis of the crystal. Spectrum (c) is a computer simulation calculated using four proton coupling constants of 26.6 G, one proton coupling constant of 23.0 G, and one proton coupling constant of 32.7 G.

extremely well-oriented liquid crystal. The coupling constants and *g* values observed in the two principal directions are given in Table I. One proton coupling constant (α^x) is highly anisotropic, whereas the other five coupling constants are very nearly isotropic. An estimate of the isotropic component (a_0^x) of α^x for both radicals, 22.1 G, is readily obtained from the relation $a_0^x = (a_z^x + 2a_{xy}^x)/3$.¹ By comparison with many known systems,^{1,5} radicals (1) and (2) are clearly π -electron radicals, and α^x arises from one proton bonded directly to the radical center. The five β -proton splittings result from the adjacent $-\text{CH}_3$ and $-\text{CH}_2-$ groups. Apparently there is a small angle of twist causing one of the methylene proton coupling constants to be accidentally equivalent, within experimental error, to the three

methyl proton coupling constants. This is not an unusual feature of trapped π -electron radicals.¹

The surprising observation is that the dominant radical in both di-*n*-butyl oxalate-urea and di-*n*-butyl malonate-urea crystals results from hydrogen atom removal from carbon atom 3 of the butanol group.⁶ The dominant radicals are not related in any way to the radicals previously observed in numerous studies of oxalic acid^{7,8} or malonic acid.⁹⁻¹¹ There are, of course, some weak unresolved lines (see Fig. 1) that may result from damage to the carboxylic acid portions of these esters. Other radicals may exist in higher concentrations for short time periods after x irradiation or at low temperatures. Nevertheless, the results presented here provide an interesting example of differences that can occur between x-ray damage in esters and the parent acids. The data also suggest a note of caution in generalizing results from a limited series of x-irradiation studies.

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‡ Alfred P. Sloan fellow.

¹ O. H. Griffith, J. Chem. Phys. **41**, 1093 (1964).

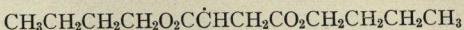
² O. H. Griffith, Proc. Natl. Acad. Sci. U.S. **54**, 1296 (1965).

³ O. H. Griffith and E. E. Wedum, J. Am. Chem. Soc. **89**, 787 (1967).

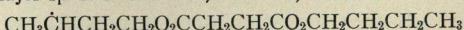
⁴ E. E. Wedum and O. H. Griffith, Trans. Faraday Soc. **63**, 819 (1967).

⁵ A. Carrington and A. D. McLachlan, *Introduction to Magnetic Resonance* (Harper and Row, New York, 1967), Chap. 7.

⁶ We have also examined the radicals formed by x irradiation of di-*n*-butyl succinate-urea inclusion crystals. In this case the radical



is the major species at 298°K; however, the radical



is also observed.

⁷ N. Rao and W. Gordy, J. Chem. Phys. **35**, 362 (1961).

⁸ G. C. Moulton, M. P. Cernansky, and D. C. Straw, J. Chem. Phys. **46**, 4292 (1967).

⁹ H. M. McConnell, C. Heller, T. Cole, and R. W. Fessenden, J. Am. Chem. Soc. **82**, 766 (1960).

¹⁰ A. Horsfield, J. R. Morton, and D. H. Whiffen, Mol. Phys. **4**, 327 (1961).

¹¹ R. C. McCalley and A. L. Kwiram, J. Am. Chem. Soc. **92**, 1441 (1970).