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*ELECTRON SPIN RESONANCE OF FREE RADICALS IN PERHYDROTRIPHENYLENE INCLUSION COMPOUNDS**

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A number of compounds have been reported in which two or more components are associated without covalent bonds and in which one of the components fits into cavities formed by the other. The cavities formed by the host molecules of these inclusion compounds may be tube-shaped, cage-shaped, or may consist of open layers.[1, 2] The best known of the tube-shaped compounds, or canal complexes, are those formed by urea.[3] X-ray crystallographic,[4] infrared,[5] dielectric absorption,[6] nuclear magnetic resonance,[7] and electron spin resonance studies[8, 9] of these compounds have been reported. Until recently, the unusual properties of the urea compounds (e.g., large variety of possible linear guest molecules and high degree of ordering of the guest molecules) have rendered them unique among crystalline inclusion compounds. In 1964, however, Farina, Allegra, and Natta[10] reported that *trans-anti-trans-anti-trans*-perhydrotriphenylene (PHTP) forms crystalline inclusion compounds with a large number of guest molecules. The crystal structure of the various PHTP inclusion compounds is hexagonal ($a = 14.3$ Å, $c = 4.8$ Å) and the precise positions of the two PHTP molecules in the unit cell have been determined. Only limited information regarding the positions of the guest molecules may be obtained from room-temperature X-ray diffraction data because of the motion of these molecules. It is of interest, therefore, to investigate selectively the guest molecules by other methods. One possible approach is to introduce dilute concentrations of paramagnetic guest molecules into the inclusion compounds and to study the motion and orientations of these free-radical "probes" by electron spin resonance (ESR). In this note we report the results of a room-temperature ESR investigation of X-ray-produced free radicals in ester-PHTP inclusion compounds.

The PHTP was prepared by hydrogenating dodecahydrotriphenylene (in heptane) by the method of Farina.[11] Single crystals of the ester-PHTP inclusion compounds were grown by slowly lowering the temperature of a solution of PHTP dissolved in the ester. Long-chain ester molecules were chosen for this preliminary study because the stable free radicals have been previously investigated in X-irradiated ester-urea inclusion compounds.[9] The ester-PHTP crystals were obtained as long hexagonal needles. The crystalline z axis is defined to lie along the needle axis and it is not necessary to specify the x and y axes other than that they are perpendicular to the basal plane. The inclusion compounds were X-irradiated at 25–40°C and the ESR spectra were obtained at 25°C with a Varian 9.5 Gc/sec spectrometer.

The spectrum of an ethyl heptanoate-PHTP crystal with the magnetic field in the xy plane is given in Figure 1. This spectrum remained unchanged as the crystal was rotated about the crystalline z axis. Otherwise, the ESR spectrum was anisotropic with respect to arbitrary rotations of the crystal in the magnetic field. This is also the case for the ethyl octanoate, ethyl nonanoate, and octyl propionate inclusion compounds. The coupling constant data are summarized in Table 1. The stable free radicals are easily identified as the radicals formed by the removal of one α proton from the parent compound ($RCH_2\dot{C}HCO_2R'$). It is important to note that *the well-resolved and symmetrical anisotropic spectra can only arise from a collection of oriented radicals.* The PHTP compounds, therefore, exhibit the same high degree of order as the urea inclusion compounds.

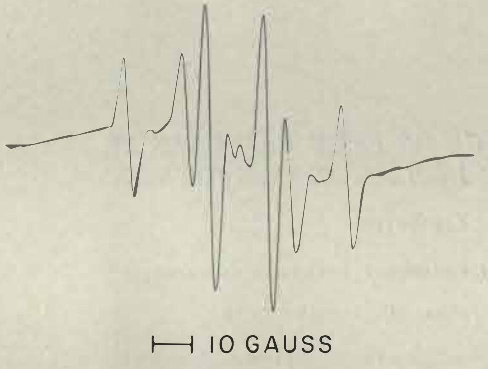

Fig. 1.—The room-temperature ESR spectrum recorded with the magnetic field in the xy plane of an ethyl heptanoate-PHTP crystal. The sharp six-line spectrum is due to the $CH_3(CH_2)_4\dot{C}HCO_2CH_2CH_3$ radical. The very broad single line in the background is evidently associated with X-ray-damaged PHTP.

TABLE 1

Proton Hyperfine Coupling Constants

Parent compound	a_z^α	a_z^β	a_{xy}^α	a_{xy}
Ethyl heptanoate	84 (85)	61	41 (41)	57
Ethyl octanoate	85 (82)	63	42 (41)	58
Ethyl nonanoate	83 (. . .)	63	41 (41)	59
Octyl propionate	. . . (84)	. . .	43 (42)	65

The radicals are those formed by the removal of one α proton from the parent hydrocarbon. The a^α and a^β are the coupling constants for the α and β protons, respectively, and xy and z denote the spectra recorded with the magnetic field in the crystalline xy plane or along the z axis. The first three radicals have two equivalent β protons each and the octyl propionate radical exhibits the three equivalent β protons characteristic of a rotating β methyl group. The estimated accuracy for the coupling constants of the ethyl heptanoate and ethyl nonanoate radicals is ±2 Mc/sec. The ethyl octanoate and octyl propionate data are accurate to within ±3 Mc/sec. The α and β coupling constants are ~71 Mc/sec with the magnetic field along the z axis of the octyl propionate crystal. This was the only spectrum exhibiting δ proton splittings. The α proton coupling constants observed for the same radicals included in urea instead of PHTP are enclosed in parentheses.

The orientation and degree of molecular motion of the guest molecules in PHTP are remarkably similar to those in urea. In both host crystals the α proton coupling constant, a^α, is isotropic in the xy plane.[12, 13] As discussed elsewhere,[9] this indicates that the amplitude of the radical motion in the crystalline xy plane exceeds ~80 degrees and the frequency of this motion is large compared to the difference in the hyperfine frequencies (~30 Mc/sec). The values of a_z^α or a_{xy}^α given in Table 1 are the same within experimental error and this suggests that the orientations of all four ester radicals included in PHTP are the same. The corresponding values of a_{xy}^α and a_z^α for these radicals in urea are 41 Mc/sec and 83 Mc/sec, respectively.[9] These two sets of values are the same within experimental error and we may conclude that the time-average spatial orientations of the $C_2—H_\alpha$ bonds are very similar, if not identical, in the two host crystals.

These data are consistent with the canal model for PHTP inclusion compounds. In particular, the ESR data suggest that the $C_2—H_\alpha$ bond (and the π orbital on C_2) of the radical lies in or near the crystalline xy plane.[9] This is consistent with a time-average extended zigzag radical conformation. The orientations of the radical in the tubular cavities are magnetically equivalent because of the large amplitude motion of the radicals about the z (tubular) axis. This motion is undoubtedly complex and low-temperature studies are planned to investigate further the motion and structure of X-ray and UV-produced radicals in PHTP inclusion compounds.

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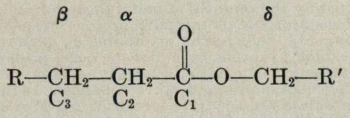
[12] The convention for labeling of protons (α, β, δ) and carbon atoms (C_1, C_2, C_3) used here is



$$R-\underset{C_3}{\overset{\beta}{CH_2}}-\underset{C_2}{\overset{\alpha}{CH_2}}-\underset{C_1}{\overset{O}{\overset{\|}{C}}}-O-\overset{\delta}{CH_2}-R'$$

[13] The room-temperature β proton coupling constants of the ethyl heptanoate, ethyl octanoate, and ethyl nonanoate radicals differ slightly in the two hosts. The two β protons of each of these radicals in PHTP are magnetically equivalent whereas in urea the two β protons of at least one radical, the ethyl octanoate radical, are magnetically distinguishable. This suggests either the deviations from a time averaged all-trans ester radical conformation are greater in urea than in PHTP or the motion of the guest radical in PHTP is slightly less hindered than it is in urea. This, however, remains only a suggestion until extensive low-temperature data become available. The β proton coupling constants of the octyl propionate radical in the two hosts are, as expected, the same within experimental error.