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. The best known of the tube-shaped compounds, or canal complexes, are those formed by urea,* X-ray crystallography,† infrared,‡ dielectric absorption,§ nuclear magnetic resonance, and electron spin resonance studies.‡ of these com-


The convention for labeling of protons (\(\beta\), \(\delta\), \(\alpha\)) and carbon atoms (C\(_1\), C\(_2\), C\(_3\)) used here is:

\[
\beta \quad \delta \\
C_1 \quad C_2 \quad C_3
\]

The room-temperature \(\beta\) proton coupling constants of the ethyl propionate, ethyl acetate, and ethyl formate radicals differ slightly in the two hosts. The two \(\beta\) protons of each of these radicals in PHTP are magnetically equivalent whereas in urea the two \(\beta\) protons of at least one radical, the ethyl acetate radical, are magnetically distinguishable. This suggests either the deviations from a time averaged all-trans type 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 \(\beta\) proton coupling constants of the ethyl propionate radical in the two hosts are, as expected, the same within experimental error.
pounds 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\(^4\) reported that trans-ester-ester-ester-urea-triphenylene (PHTP) forms crystalline inclusion compounds with a large number of guest molecules. The crystal structure of the various PHTP inclusion compounds is hexagonal \((a = 14.3 \AA, c = 4.8 \AA)\) 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 hexane) 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.\(^{12}\) The ester-PHTP crystals were obtained as long hexagonal needles. The crystallographic 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 G Hz/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 \(\alpha\) proton from the parent compound \((\mathrm{CH}_3\mathrm{CH}_2\mathrm{CO})_n\mathrm{H}\). It is im-

![Figure 1](image-url)

FIG. 1.—The room-temperature ESR spectrum recorded with the magnetic field in the \(xy\) plane of an ethyl heptanoate-PHTP crystal. The \(600 \mathrm{MHz}(24.4 \mathrm{GHz})\) field is parallel to the \(\mathrm{CH}_3(\mathrm{CH}_2)_n\mathrm{COCH}_3\mathrm{CH}_2\) radical. The very broad single line in the background is evidently associated with X-ray-damaged PHTP.

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.

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 \(\alpha\) proton coupling constant, \(a_{\alpha}\), is isotropic in the \(xy\) plane.\(^{15,16}\) As discussed elsewhere,\(^4\) 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 in-plane hyperfine frequencies (~30 Mc/sec). The values of \(a_{\alpha}\) and \(a_{\beta}\) 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 \(a_{\alpha}\) and \(a_{\beta}\) for these radicals in urea are 41 Mc/sec and 83 Mc/sec, respectively.\(^6\) These two sets of values are the same within experimental error and we may conclude that the time-average spatial orientations of the \(\mathrm{C}_2\)-H 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 \(\mathrm{C}_2\)-H bond (and the \(\pi\) orbital on \(\mathrm{C}_2\)) of the radical lies in or near the crystalline \(xy\) plane.\(^6\) 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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\(^8\) Unlike molecules, notably ureas, form similar compounds.\(^4\)


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\[ a - b - c \]

The room-temperature \( \beta \) proton coupling constant of the ethyl isopropyl, ethyl isobutyl, and ethyl isooctyl radicals differ slightly in the two hosts. The two \( \beta \) protons of each of these radicals in PHTP are magnetically equivalent whereas in urea the two \( \beta \) protons of all but one radical, the ethyl isooctyl radical, are magnetically distinguishable. This suggests either the deviations from a true average show smaller radial dispersion 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 \( \beta \) proton coupling constant of the octyl propionate radical in the two hosts are, as expected, the same within experimental error.