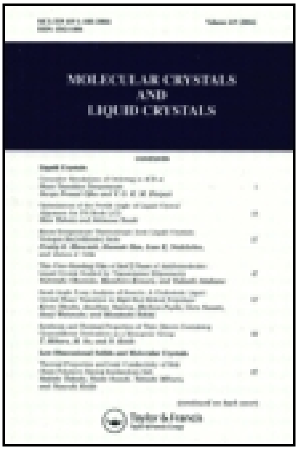

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Paramagnetic Centers in X-irradiated Chrysene Single Crystals

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Paramagnetic Centers in X-irradiated Chrysene Single Crystals

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Abstract—An X-irradiated single crystal of chrysene, $C_{18}H_{12}$, has been investigated by electron spin resonance to determine the types of stable free radicals formed by the radiation. Previous investigations of other aromatic hydrocarbons (benzene, naphthalene, and anthracene have indicated the formation of two radical types simultaneously, hydrogen abstraction radicals and hydrogen addition radicals.

The single crystal was grown at room temperature from a solution of chrysene in dimethylformamide. Chrysene belongs to a monoclinic crystal system, forms (001) platelets when grown from solution, and is easily oriented with the aid of a polarizing microscope. The ESR spectrometer was operated at approximately 9.5 GHz with 100 KHz field modulation and phase sensitive detection. The spectra was recorded at 10° intervals for rotation of the magnetic field about each of the three orthoganal axes, *abc**.

The spectrum of chrysene exhibited a triplet characteristic, similar to that previously reported for benzene, naphthalene, and anthracene. The hyperfine structure in the spectrum has been interpreted as a doublet-triplet-triplet spectrum with the doublet exhibiting the anisotropic characteristics that are associated with an α-proton interaction. The hyperfine spectrum is superimposed on a poorly resolved isotropic doublet. The hyperfine spectrum has been interpreted as being associated with a hydrogen addition free radical, and the poorly resolved doublet has been assigned to a hydrogen abstraction radical. The interpretation of the spectrum is consistent with the results and conclusions that have been reported for benzene, naphthalene, and anthracene.

1. Introduction

ESR investigations of the effects of ionizing radiation on the aromatic hydrocarbons, benzene, naphthalene, and anthracene, indicate that stable hydrogen abstraction radicals and hydrogen addition radicals are simultaneously present in the materials following irradiation.(1–16) The results of the investigation described in the present paper indicate that similar radicals are also present in X-irradiated single crystal chrysene, another of the aromatic hydrocarbons.

2. Experimental

Powdered chrysene was obtained from the Eastman Chemical Company, and single crystals were grown by slow evaporation of a saturated solution of chrysene in dimethylformamide at room temperature. A single crystal of chrysene suitable for ESR investigation was irradiated at room temperature with 50 kvp, 40 ma X-rays.

Chrysene single crystals are monoclinic and belong to the space group I2/c. The cell constants are: $a = 8.39$ Å, $b = 6.20$ Å, $c = 25.20$ Å, and $\beta = 116.2°$; there are four molecules per unit cell.(17) Chrysene single crystals grow in (001) platelets,(18) and they are easily oriented with the aid of a polarizing microscope. The set of orthogonal axes abc^* was chosen for the ESR investigation.

The ESR spectrometer was operated at approximately 9.5 GHz with 100 KHz field modulation and phase sensitive detection. All spectra were recorded at room temperature. The interval of rotation about each of the orthogonal axes was 10°.

3 Results

Representative spectra obtained are shown in Figs. 1(a), 1(b), and 1(c), where the magnetic field is parallel to the a-, b-, and c^*-axes, respectively. The spectra obtained when the magnetic field was approximately parallel to the a- or b-axes exhibited intensity ratios similar to those of a triplet, although the intensity of the center of the spectrum was greater than that expected for a 1 : 2 : 1 triplet. Near the a- and b-axes the center of the spectrum showed little, or no hyperfine structure, although hyperfine structure was evident to either side of the center. Figure 1(c) shows that when the magnetic field was near the c^*-axis the center exhibited a broad doublet character; the hyperfine structure which was observed in orientations near the a- and b-axes was more poorly resolved near the c^*-axis.

Similar spectra have been reported for benzene, naphthalene, and anthracene; in each of those cases it was suggested that the excess

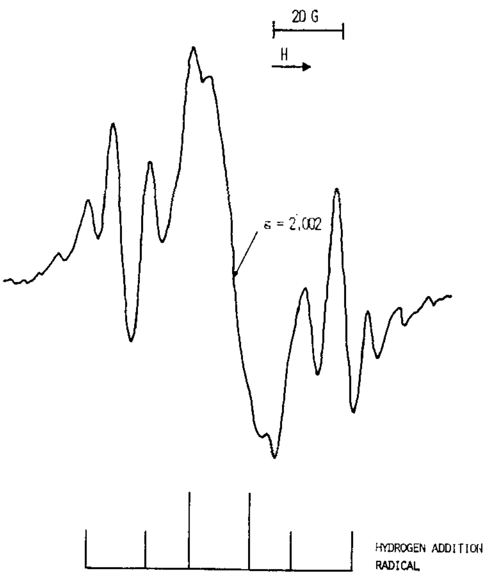

Figure 1(a) The spectrum of chrysene for H parallel to the *a*-axis.

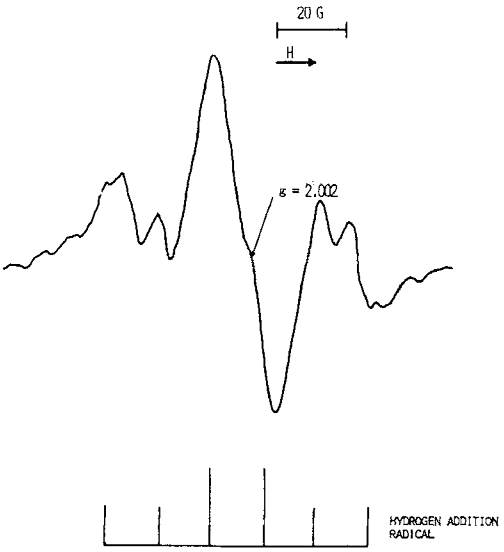

Figure 1(b) The spectrum of chrysene for H parallel to the *b*-axis.

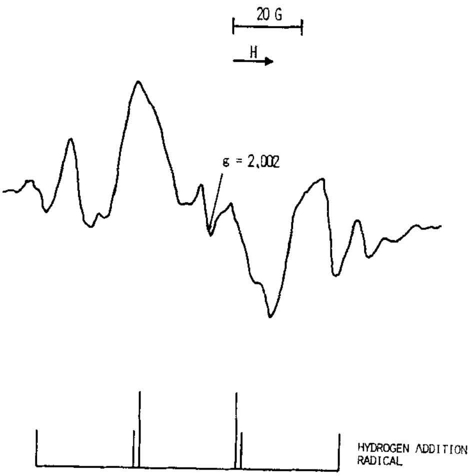

Figure 1(c) The spectrum of chrysene for H parallel to the c^*-axis.

intensity of the center indicated the presence of more than one radical type. Cook *et al.*(19) observed a similar spectrum for irradiated single crystal cytosine-monohydrate; they reported that when the microwave power was increased the central portion of the spectrum saturated at a different rate than the hyperfine structure. They concluded that at least two different radical species were therefore present. It was observed that for chrysene the center of the spectrum saturated more slowly than the outer hyperfine lines as the microwave power was increased. It is also possible that when two or more radical species are present, one will decay faster than the other(s) when the crystal is stored at room temperature for some time. Therefore, a change in the number of lines in the spectrum or a change in the intensity ratios of the lines would indicate that two or more radical types were present and were decaying at different rates. However, the spectrum of the chrysene crystal investigated remained the same more than two years after the crystal was irradiated. Based on the results for benzene, etc. and the observed power saturation results, it was concluded that at least two radical species are produced in single crystal chrysene by X-irradiation. Furthermore, it has been concluded that the broad, poorly resolved, central doublet is associated with one radical type present and that the better resolved spectrum is associated with another specie.

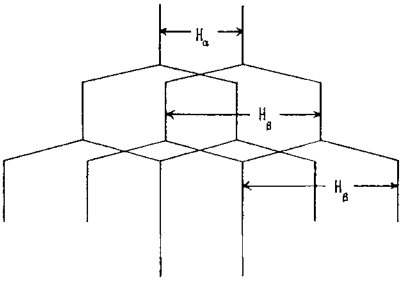

Figure 2. Formation of the doublet-triplet hyperfine spectrum for H parallel to the *a*-axis.

It was observed that as the magnetic field was rotated about each of the three axes, *a*, *b*, and *c**, the separation between six of the hyperfine lines behaved in a manner similar to that reported in the single crystal studies of naphthalene,(11–14) anthracene,(16) and cytosine-monohydrate.(19) The positions and relative intensities of these lines are shown below the spectra in Fig. 1. The observed anisotropy and intensity ratios suggest an anisotropic coupling between the unpaired spin density and one α-hydrogen atom, superimposed on the approximately isotropic coupling of part of the free spin density with two equivalent β-hydrogen atoms. The β-coupling is approximately 30 G. The six spectral lines would be formed as shown in Fig. 2, where the α-coupling is about 15 G. In some orientations another triplet splitting of approximately 5 G is also evident.

For each plane of rotation, the α-coupling was measured between each outer, well resolved, pair of lines, as the pair of lines in the center were generally obscured by the broad central doublet. Figures 3(a), 3(b), and 3(c) show the variation of the α-splitting as a function of orientation with respect to the magnetic field in the *ab*-, *bc**-, and *c***a*-planes, respectively. The *ab*-plane is almost perpendicular to the plane of the molecule; one would therefore expect only a small anisotropy in the α-splitting in the *ab*-plane. The small variation of the α-splitting, the expected site splitting in the *ab*-plane, and the complexity of the spectrum account for the small number of experimental data points in Fig. 3(a).

The α-coupling tensor determined for the radical associated with the hyperfine spectrum is given in Table 1, along with the principle

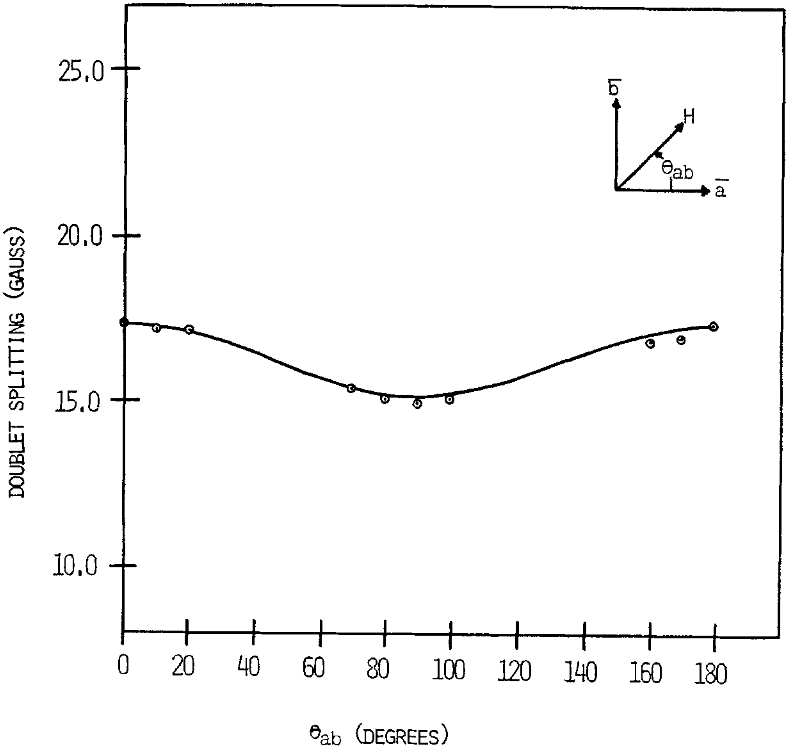

Figure 3(a) Anisotropic doublet splitting *vs.* angle between H and the *a*-axis for rotation in the *ab*-plane.

values and the directional cosines. The isotropic component of the interaction is −20.03 G; and the anisotropic components are +2.81, +5.45 and −8.26 G. The negative sign for the principal values is inferred from the theory.(20,21)

For the space group I2/c one expects to observe contributions to the spectra from two magnetically non-equivalent sites, unless the magnetic field is perpendicular to or parallel to the *b*-axis. For the spectra obtained from chrysene, this site splitting apparently only caused some broadening of the lines, making it difficult to accurately measure the position of the lines at many orientations and adding to the general complexity of the spectra, as has been noted.

The directional dependence of the *g*-value at the center of the spectrum or the *β*-hydrogen interaction has not been investigated.

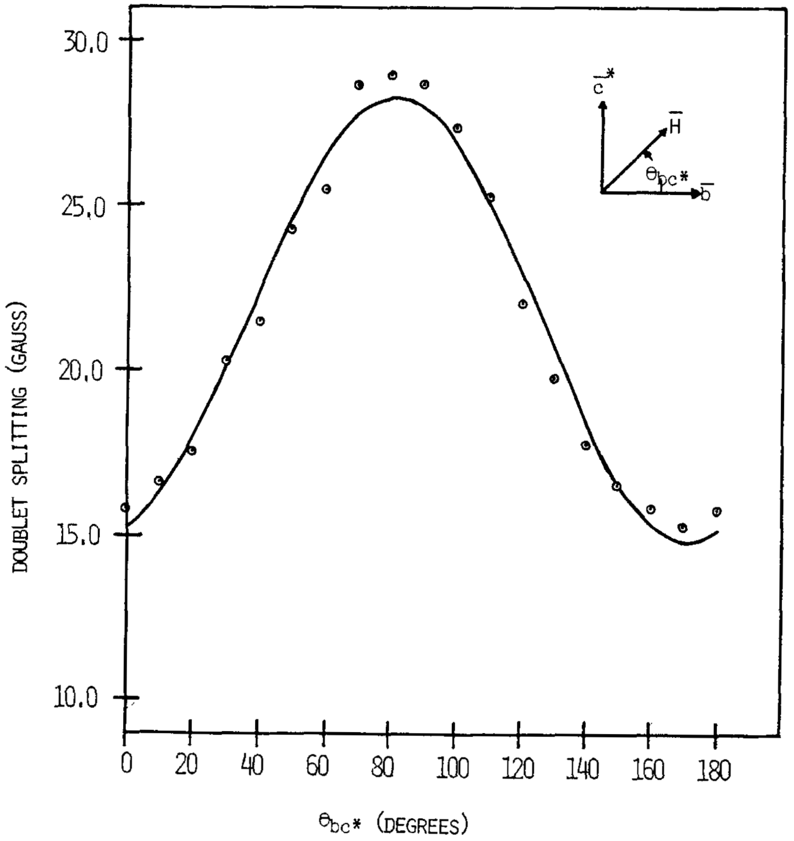

Figure 3(b) Anisotropic doublet splitting *vs.* angle between H and the *b*-axis for rotation in the *bc**-plane.

However both the *g*-value and *β*-coupling were very nearly isotropic The measured *g*-value was 2.002.

4. Discussion and Conclusions

It is inferred from the anisotropy of the spectrum, from the triplet characteristics exhibited by the spectrum, and from the results of investigations on related compounds (benzene, etc.) that hydrogen addition radicals are present in irradiated chrysene. The principal values determined for the *α*-hydrogen interaction (-17.22 G, -14.58 G, -28.29 G) are in good agreement with those generally

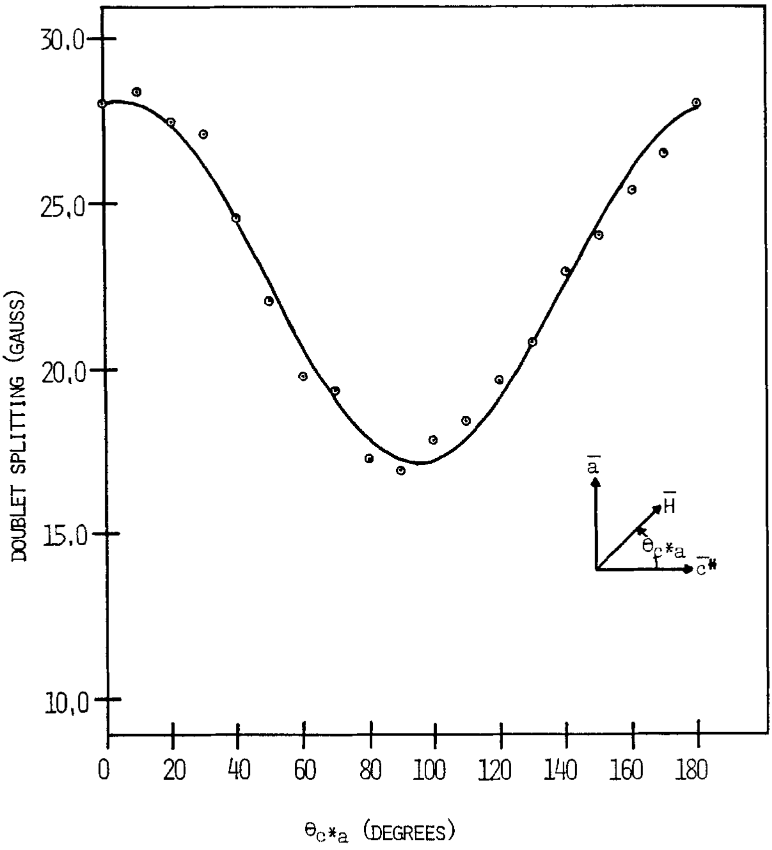

Figure 3(c) Anisotropic doublet splitting *vs.* Angle between H and the c^*-axis for rotation in the c^*a-plane.

found for carbon-centered π-electron radicals.$^{(22)}$ The signs of the principal values have been assumed to be negative on theoretical grounds.$^{(20,21)}$ From McConnell's relationship,$^{(23)}$ the unpaired spin density on the central carbon atom has been calculated to be 0.80 ± 0.03.

It is expected$^{(21,24)}$ that the principal axes of the coupling tensor corresponding to the least negative, intermediate, and most negative principal values will be parallel to the C—H bond, normal to the radical plane, and in the radical plane but perpendicular to the C—H bond, respectively. Thus, the principal axis corresponding to a coupling of − 14.58 G should be parallel to the C—H bond. Figure 4

TABLE 1 The Hyperfine Tensor, Principal Values, Anisotropic Components of the Principal Values, and Direction Cosines Found for the α-Proton Interaction in the Chrysene Hydrogen Addition Radical

	Hyperfine tensor in the abc^* axial system (Gauss)			Principal values (Gauss)	Anisotropic components (Gauss)	Direction cosines		
	17.27	−0.09	0.87	−17.22	+2.81	0.9932	0.0870	0.0769
(−)	−0.09	14.93	2.09	−14.58	+5.45	−0.0980	0.9832	0.1538
	0.87	2.09	27.89	−28.29	−8.26	−0.0622	−0.1603	0.9851

shows the radical structure consistent with these observations. From the direction cosines determined for the principal axis of the α-hydrogen interaction, high spin density can be assigned to either C1(C7) or C5(C11) assuming a slight rearrangement in the bond direction in the damaged molecule. The assignment of the high spin density to C1(C7) is based on the results of molecular orbital calculations.(25) Addition of hydrogen to C6(C12) would result in a phenanthrene-like residue with the spin located at C5(C11), but addition of the hydrogen to C2(C8) with the spin located at C1(C7) leaves a 2-phenyl naphthalene-like residue which would be expected to be more stable than the phenanthrene by about 6 kcal.(26) Since there was no change in the ESR spectrum after more than two years of aging at room temperature the thermodynamically more stable radical specie is assumed.

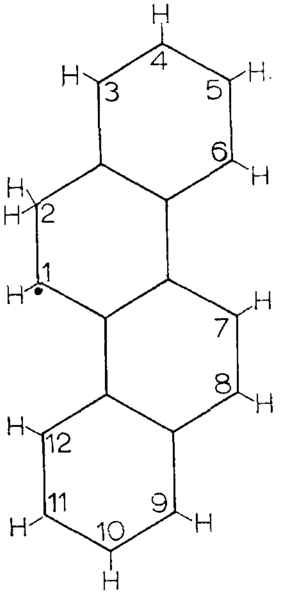

Figure 4. The hydrogen-addition radical in irradiated chrysene.

It is also inferred from the intensity ratios, the poorer resolution in the center of the spectrum, the power saturation results, and the previous results on benzene, etc. that hydrogen abstraction radicals are present. However, it has not been possible to determine from the spectra the distribution of the free electron spin or the carbon atom from which a hydrogen nucleus has been removed.

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