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X- and γ-Radiation Damage to Single Crystal Anthracene

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X- and γ-Radiation Damage to Single Crystal Anthracene†

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Recently Blum, Mattern, Arndt, and Damask[1] reported the production of both optically absorbing and paramagnetic species in the gamma radiolysis of crystals of anthracene. They found no such behavior on exposure of this material to 50 keV X-rays.

Since for both 50 keV X-rays and Co^{60} gamma rays the majority of chemical events following the primary interaction of the photon with the material are produced by the secondary electrons, it would be quite surprising to find a qualitative difference between these two radiations. Quantitative differences may occur due to change in the linear energy transfer (LET) of the secondary electrons, but in aqueous systems in this range of LET, the product yields vary only by about 30%.[2]

Their conclusion that there is a qualitative difference in the behavior between Co^{60} gamma and 50 keV X-radiolysis, of enormous importance to any theory of radiation chemistry, has led us to re-examine the behavior of anthracene toward low energy X-radiation.

A single crystal of anthracene obtained from the Harshaw Chemical Company was exposed in air to radiations from an X-ray tube operated at 50 kV peak, and filtered to remove radiation below 6 keV, for times sufficient to give doses of 2×10^6 and 8×10^6 rads. This crystal, 0.2 cm thick and 0.5 cm^2 area, after 8×10^6 rads exhibited an increased optical absorption in the range 4200–6000 Å similar in nature to that observed by Blum *et al.*,[1] for Co^{60}

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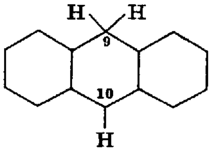
γ-radiolysis. The optical density change at 4600 Å was measured to be 0.1 compared to 0.08 calculated from their data obtained at 1.48×10^8 rads, assuming linear increase of optical density with dose. This is, within the relative errors of the two measurements, the same value.

E.S.R. measurements were performed on this same crystal and signals were detected for doses as low as 2.2×10^6 rads. The spectrum obtained at a dose of 8×10^6 rads is identical to that found following gamma-radiolysis. A high purity crystal obtained from R. Arndt gave nearly the same optical spectrum and an identical E.S.R. spectrum to the Harshaw crystal.

We would like to suggest that the crosslinked radical proposed in Blum *et al.*,[1] is unlikely to be responsible for the observed signal. Ingalls and Kivelson[3] have shown that radicals derived from aromatic systems by ionizing radiation are often assignable to substituted cyclohexadienyl moieties. Most radiolyses of hydrocarbons result in radicals derived from the parent hydrocarbons by simple dissociations and additions and do not involve major rearrangements of the type suggested by the previously proposed structure.

A radical derived from anthracene by hydrogen atom addition to the 9 position in anthracene, dibenzo cyclohexadienyl(I), can adequately account for the observed spectrum. Nearly equal interactions with the two protons on carbon 9 and the single proton on carbon 10 can explain the major splittings observed while unresolved hyperfine interaction with the remaining eight ring protons is responsible for the rather large line widths.



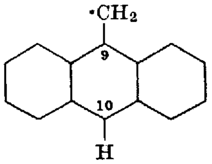
(I)

A simple molecular orbital calculation of the spin densities in I was performed and isotropic hyperfine couplings calculated using

McConnell's relationship[4] and the observed coupling parameters of Fessenden and Schuler.[5]

The calculated splitting from the lone proton at position 10 was 12.4 gauss and the splittings calculated for the two protons at position 9 were 12.1 gauss. These splittings are in reasonable agreement with the isotropic part of observed axial Hamiltonian of Blum *et al.*, 14.8 gauss for three nearly equivalent protons.

In contrast to anthracene, the most common radiation chemical product in 9-methyl anthracene would involve removal of a methyl proton. This radical also is expected to have three almost equivalent protons which coincidentally have about the same isotropic hyperfine interaction as (I). This explains the similarity in *powder* spectra observed by Blum *et al.*, for anthracene and 9-methyl anthracene.



(II)

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2. See, for example, Chapiro, A., *Radiation Chemistry of Polymeric Systems*, Interscience Publishers, pp. 59–62.
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