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Electron Spin Resonance of Stable Aromatic  
Radical Intermediates in Pyrolysis

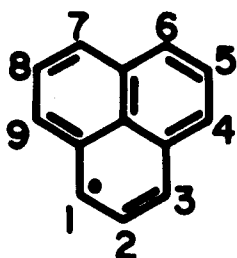
I. C. Lewis and L. S. Singer

Union Carbide Corporation  
Carbon Products Division  
Parma Technical Center  
Parma, Ohio 44130

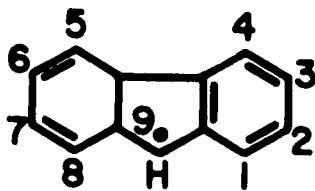
ABSTRACT

This paper presents the results of electron spin resonance measurements on several types of stable aromatic free radicals suspected as intermediates in carbonization. Previous observations of ESR hyperfine structure during the initial stages of carbonization have indicated that stable, neutral radicals are produced by thermal bond cleavage and rearrangement of the starting aromatic molecules.<sup>(1)</sup> For example, the phenalenyl (perinaphthyl) radical (I) has been observed to form during the pyrolysis of a number of organic starting materials.<sup>(1,2)</sup>

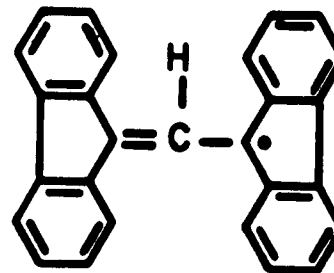
We have prepared and measured the ESR spectra of the following stable neutral radicals: phenalenyl (I), 1-methylphenalenyl, 1-phenylphenalenyl, fluorenyl (II), 9-phenylfluorenyl, and biphenyleneallyl (III).



(I)



(II)



(III)

The radicals were produced from organic compounds of known structure by simple dissociation reactions at temperature considerably below ordinary carbonization temperatures.

Phenalenyl (I) substituted by either a methyl or phenyl group at the 1-position shows the same high stability as the unsubstituted phenalenyl radical. This substitution apparently has little effect on the spin densities and, thus, on the reactivities of the other positions in the molecule. The ESR coupling constants also provide information concerning the planarity of the substituted phenalenyls.

The fluorenyl radical (II) can be prepared by dissociation of its dimer at a temperature higher than 250°C. Phenyl substitution at the 9-position results in

large phenyl proton splittings, implying essential planarity of the phenyl and fluorenyl ring systems.

The high thermal stability of the biphenyleneallyl radical (III) is consistent with the fact that it can be formed at high temperatures by the rearrangement of several different substituted fluorene derivatives. Our coupling constants for biphenyleneallyl agree with those reported by Hausser<sup>(3)</sup> but are in very poor agreement with theory.

The reactivity, conformation, and role of these radicals in subsequent carbonization reactions are discussed.

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- (1) I. C. Lewis and L. S. Singer, Carbon 2, 115 (1964).
  - (2) J. E. Bennett, Proc. Chem. Soc. 144 (1961).
  - (3) K. H. Hausser, Z. Naturforsch. 17a, 158 (1962).