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### **Title**

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### **Authors**

Sogo, Power B.  
Nakazaki, Masao  
Calvin, Melvin

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ABSTRACT

The electron spin resonance spectrum of the perinaphthene free radical is reported and a discussion of electron spin density in this radical is given.

THE FREE RADICAL FROM PERINAPHTHENE\*

Power B. Sogo, Masao Nakazaki,\*\* and Melvin Calvin

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During the course of investigation of the isomerization reactions of perinaphthene, using carbon-14,<sup>1</sup> a solution of perinaphthene in carbon tetrachloride was prepared for proton magnetic resonance examination. The fresh sample, sealed in air, was a colorless solution and produced a clear proton spectrum confirming the presence of two distinct vinylic protons, one methylene group and six aromatic-type protons.

When the solution had stood for several hours, the surface layers began to show a yellow color and the proton spectrum lost its resolution. This suggested the possibility of the creation of magnetic material, and an examination of the partly colored solution in the electron spin resonance spectrometer clearly demonstrated the presence of a complex spectrum associated with the yellow part of the solution but absent in the colorless part. This spectrum has now been examined over a period of several months, the solution being mixed in the interim, and its most recent appearance is reproduced in Fig. 1. The earlier spectra, which appeared within a few days after the solutions were prepared, are very similar but of somewhat smaller intensities. It is clear that the radical is quite stable under these conditions.

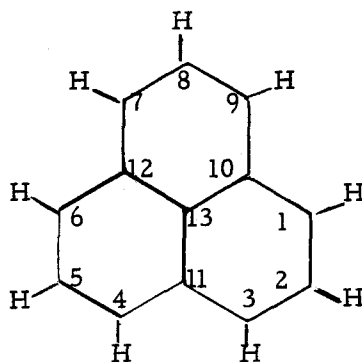
An examination of the spectrum reveals that it may be described in terms of seven lines in the ratio 1:6:15:20:15:6:1; each of these seven lines is further split into a quadruplet in the ratio of 1:3:3:1. This spectrum is quite readily interpreted in terms of the symmetrical free radical that would result from perinaphthene by the removal of one hydrogen.

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\*\* Visiting professor from Institute of Polytechnics, Osaka City University, Osaka, Japan. Present address: Department of Chemistry, Wayne State University, Detroit 32, Michigan.

<sup>1</sup> M. Nakazaki, to be published.



Unsuccessful attempts to prepare this radical have been described earlier.<sup>2</sup>

The construction of the first-order valence-bond resonance forms clearly shows the presence of the odd electron on the six symmetrically located positions, 1, 3, 4, 6, 7, and 9, thus providing a primary hyperfine interaction with six equivalent protons and accounting for the septet with the larger splitting of about 7.3 oersteds. Second-order or excited valence-bond resonance forms would be required to permit the odd electron to reside on the remaining three symmetrically located protons, 2, 5, and 8, thus accounting for the quartet with the smaller splitting of about 2.2 oersteds. A simple LCAO-MO construction yields exactly the same qualitative result for the electron distribution in the highest occupied state.<sup>3</sup>

The splitting values have been used to estimate electron spin densities at the corresponding protons, assuming the splitting factor of approximately 500 for the full value of an s-electron on a hydrogen atom.<sup>4,5</sup> In order to get any spin densities at an aromatic proton, an interaction between the pi orbitals and the CH-bond sigma orbitals must be assumed, and a quantitative estimation of this has been made<sup>6</sup> which has led to the value of 28 oersteds as the spread corresponding to the presence of a unit spin density in the pi orbital of an aromatic CH group. This has indeed been

<sup>2</sup> V. Boekelheide and M. Goldman, J. Am. Chem. Soc. 76, 604 (1954).

<sup>3</sup> W. D. Gwinn, private communication.

<sup>4</sup> S. I. Weissman, J. Chem. Phys. 25, 890 (1956).

<sup>5</sup> Tuttle, Ward, and Weissman, J. Chem. Phys. 25, 189 (1956).

<sup>6</sup> H. S. Jarrett, J. Chem. Phys. 25, 1289 (1956).

found to be so in a number of charged aromatic radicals such as benzene negative ion,<sup>7</sup> naphthalene negative ion,<sup>5</sup> anthracene negative ion,<sup>8</sup> and biphenyl negative ion.<sup>8</sup> The neutral radical as triphenyl methyl<sup>9</sup> has a minimum spread due to proton hfs of ~30 oersteds, while the radical spectrum described here has a minimum spread of 49 oersteds.

There is certainly less than unit electron spin density on the three phenyl groups of triphenylmethyl. This is further indicated by the 22-oersted splitting<sup>10</sup> induced by the C<sup>13</sup> in the methyl carbon, suggesting a rather large spin density on this atom. It therefore seems fairly certain that the nature of the pi-sigma interaction in this radical, as well as in the perinaphthenyl radical, must be very different from what it is in the aromatic negative-ion radicals.

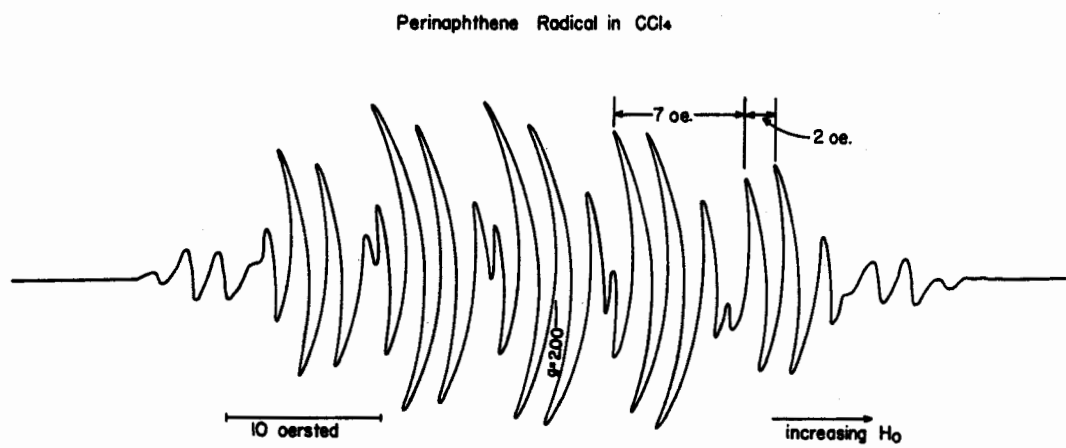
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<sup>7</sup> S. I. Weissman, J. Chem. Phys. in press.

<sup>8</sup> E. deBoer, J. Chem. Phys. 25, 190 (1956).

<sup>9</sup> H. S. Jarrett, J. Chem. Phys. 21, 761 (1953).

<sup>10</sup> S. Weissman and J. C. Sowden, J. Am. Chem. Soc. 75, 503 (1953).



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Fig. 1. Electron spin resonance spectra of perinaphthene radical in carbon tetrachloride.