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ESR HYPERFINE STRUCTURE IN N-PICRYL-9-AMINOCARBAZYL

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In the course of an investigation of the magnetic properties of the stable organic radicals, we remeasured the electron spin resonance (ESR) spectrum of N-picryl-9-aminocarbazyl (PAC) radical in solution and in polycrystal.

PAC is a neutral radical, whose structure is similar to 1,1-diphenyl-2-picrylhydrazyl (DPPH) radical. The chemical structure of PAC is given in FIG.1.

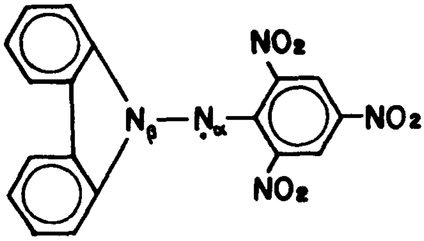

FIG.1
N-picryl-9-aminocarbazyl

The hyperfine structure of PAC in solution was first investigated by Kikuchi and Cohen$^{(1)}$, and also by Jarrett$^{(2)}$. They reported that the hyperfine spectrum consisted from seven lines with the intensity ratio of approximately 1:1:2:1:2:1:1, and was attributed to the isotropic hyperfine interaction of two nitrogens with an unpaired electron. Synthesizing resonance spectra with various parameters, Lord and Blinder$^{(3)}$ determined the following hyperfine coupling constants, that is, $A_{N(\alpha)}$ = 10.2 Gauss, $A_{N(\beta)}$ = 5.8 Gauss.

PAC in solution is relatively unstable than the polycrystalline form. In particular, PAC in etherial solvents (e.g. tetrahydrofuran, etc.) is so unstable

FIG.2
ESR spectrum of PAC in dilute chloroform solution at room temperature.

that the violet solution changes at once into yellow-brown color which is characteristic to N-picryl-9-aminocarabzole (PACH), the precursor substance. Among various organic solvents so far investigated, the best was chloroform. A fairly well resolved spectrum was obtained in the very dilute chloroform solution of PAC following the same procedure as reported by one of the authors (YD)$^{(4)}$, while in relatively high concentration, the obtained spectrum agreed qualitatively with the earlier results$^{(1-3)}$ (FIG.2).

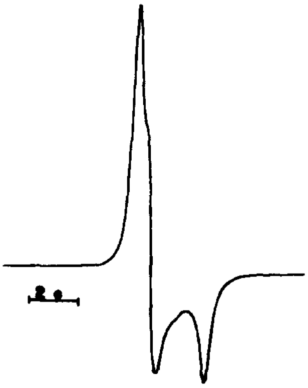

FIG.3
ESR spectrum of PAC powder at room temperature.

PACH was synthesized from N-aminocarbazole and picrylchloride$^{(5)}$, followed by the recrystallization from chloroform-ethanol mixed solvent (about 1:1), and its melting point was 239°- 240°C. PACH was oxidized to PAC with PbO_2 in absolutely dried chloroform using Na_2SO_4 as an drying reagent. As soon as this solution was purified by the column-chromatographic method employing activated alumina as an adsorber, the solvent was thoroughly evaporated to give the powdered sample. Dissolving PAC powder in chloroform in vacuo, then the solution was completely degassed.

The observed spectrum in very dilute solution (approximately 10^{-4}-10^{-5} M) (FIG.2) is very complicated by the overlapping of the hyperfine splittings due to many sorts of nuclei. The following hyperfine coupling constants were adopted to reconstruct the observed spectrum by an ESR simulater. Perfect agreement was not obtained, but the coupling constants shown below were the best fit. The smallest splittings (0.4 Gauss) might be due to the three nitrogen atoms on the picryl skelton.

$$A_{N(\alpha)} = 11.1 \text{ Gauss}, \quad A_{N(\beta)} = 6.0 \text{ Gauss},$$
$$A_H = 2.6 \text{ Gauss}^{(6)}, \quad A_{N(pic)} = 0.4 \text{ Gauss}^{(7)}.$$

The isotropic g-value of PAC in solution was determined as 2.0032 from the measurement of the field intensity at the center of the ESR spectrum. The ESR spectrum of PAC powder prepared by the aforementioned method was anisotropic and gave the three principal values of g-tensors as 2.0022, 2.0034 and 2.0039 (FIG.3). The average value of the three ones is 2.0032, which agreed with the one in solution.

All measurements were made by a JES-3B type ESR spectrometer equipped with 100kc/s field modulation and a JES 12 inch magnet.

REFERENCES AND FOOTNOTES

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(6) H in A_H denotes the four ortho- and para-hydrogen atoms in the carbazyl skelton.

(7) N(pic) in $A_{N(pic)}$ denotes the three nitrogen atoms of NO_2 groups in the picryl skelton.