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BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (7), 2141—2142 (1979)

ENDOR Spectrum of Some Dihydro-1,4-dithiin Cation Radical

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(Received September 30, 1978)

Synopsis. The ENDOR spectrum of the 2,3-diphenyl-5,6-dihydro-1,4-dithiin cation radical, which was prepared with $AlCl_3$ in dichloromethane solution, has been observed. The spin density distribution of the new radical was also discussed and compared with the MO calculation.

ESR detections of the intermediate cation radical (g=2.0070+0.0005) formed by thallium(III) nitrate oxidation of 2,3-diphenyl-5,6-dihydro-1,4-dithiin have been previously reported.[1] Several ESR studies of 1,4-dithiin cation radicals have been published,[2] but no detailed data on the spin density distribution of the dihydro-1,4-dithiin cation radical have been given. In the present work, ENDOR observations are carried out for the intermediate cation radical produced by one electron oxidation of 2,3-diphenyl-5,6-dihydro-1,4-dithiin, and the spin density distribution of the new radical is investigated.

Experimental

The synthesis of materials has been described elsewhere.[1] Cation radicals of 2,3-diphenyl-5,6-dihydro-1,4-dithiin were prepared using thallium(III) nitrate as the oxidant. It was found, however, that the identical cation radical generated by $AlCl_3$ oxidation in CH_2Cl_2 showed a rather enhanced stability as compared with the case of thallium(III) oxidation, and no important change in the detailed hyperfine structures could be detected in the ESR spectrum. ENDOR observations were applied to this solution using a JEOL-type EX-EDX-1 spectrometer under the operating conditions similar to those described previously.[3]

Results and Discussion

Figure 1 shows the ENDOR spectrum of 2,3-diphenyl-5,6-dihydro-1,4-dithiin cation radical prepared with $AlCl_3$ oxidation in CH_2Cl_2. The four ENDOR signals (14.31, 14.76, 14.90, and 15.11 MHz) seen in the vicinity of the free proton frequency can be ascribed to the splitting due to the phenyl groups, with reference to the MO calculation of the spin densities summarized in Table 1. The ENDOR signals (17.20 and 22.73 MHz) detected at higher NMR frequency were safely assigned to either equatorial and axial protons in bridged methylene, as discussed later.

McLachlan's MO calculations (λ=1.0) were carried out using the following parameters: $\alpha(S)=\alpha(C)+1.0\beta$, $\alpha(CH_2)=\alpha(C)+2.0\beta$, $\beta(S\text{–}C)=0.6\beta(C\text{–}C)$, $\beta(S\text{–}CH_2)=0.4\beta(C\text{–}C)$, $\beta(C\text{–}\phi)=0.75\beta(C\text{–}C)$, and $\beta(CH_2\text{–}CH_2)=0$, where $\alpha(S)$ and $\alpha(CH_2)$ are the Coulomb integrals of sulfur atoms and of methylene carbon atoms, $\beta(S\text{–}C)$, $\beta(S\text{–}CH_2)$, and $\beta(C\text{–}\phi)$ are the resonance integrals defined for sulfur-ethylene carbons, sulfur-methylene carbons, and to ethylene bridging phenyl carbons, respectively. The present ENDOR measurement resolved four different hyperfine splittings, which could be assigned to the phenyl protons. An appropriate

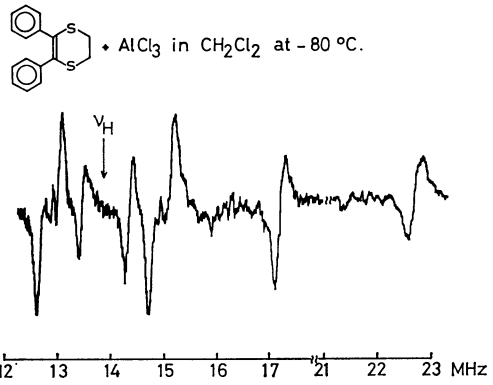
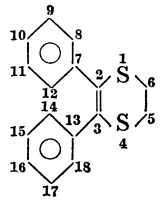


Fig. 1. Higher frequency half of ENDOR spectrum of 2,3-diphenyl-5,6-dihydro-1,4-dithiin cation radical. ν_H: free proton frequency.

TABLE 1. SUMMARY OF CALCULATIONS

	Calcd		Exptl	
	ρ_i	hfs/G	ρ_i[c]	hfs/G
1, 4	0.2195	—	—	—
2, 3	0.2241	—	—	—
5, 6	0.0084	6.336[d] 2.329[d]	—	6.339 2.383
7, 13	0.0175	—	—	—
12, 14	0.0321	0.879[c]	0.0336	0.894[a]
8, 18	0.0319	0.874[c]	0.0278	0.741[a]
10, 16	0.0296	0.810[c]	0.0241	0.643[a]
11, 15	0.0143	0.384[c]	0.0120	0.323[b]
9, 17	0.0139	0.373[c]		

a) The positions on the phenyl groups were tentatively assigned by MO calculation. b) The ENDOR spectrum can not resolve the difference in the hyperfine splittings of the meta-positions.



c) $a_i=|-12\rho_i^2-27\rho_i|$.

d) The axial and equatorial protons (see Text).

space filling model suggests that a steric repulsion may work between sterically approaching ortho protons (12- and 14-positions) in phenyl groups. This causes different hyperfine splittings at the positions 8 and 12, and 14 and 18. Taking account of a perturbation on the spin densities affected by the steric interaction, a slightly electro positive value was assumed for the Coulomb integrals at the ortho positions, that is, α(C-12)=α(C-14)=$\alpha-0.1\beta$, in the same manner as has been applied to the *o*-terphenyl anion radical.[4] The MO spin densities on the phenyl groups thus calculated gave good agreement with the experimental spin densities estimated from the Colpa-Bolton's equation,[5] as shown in Table 1. It is noteworthy that the MO spin densities on the sulfur atom (0.2195) are close to those of dithiin sulfur atoms determined from the extra splitting of S^{33} (0.289).[2] This suggests that the dihydrodithiin cation radicals can be regarded to be one of the π-radicals in nature.

Both axial and equatorial proton splittings (a^{ax}, a^{eq}) are calculated in terms of the $\cos^2\theta$ rule:

$$a^{ax} = B\rho_S \cos^2\theta,$$
$$a^{eq} = B\rho_S \cos^2(60-\theta),$$

where B is the hyperconjugation parameter between the sulfur and the methylene group, ρ_S is the spin density on the sulfur atoms, and θ is the usual dihedral angle between sulsur p-orbital and sp^3-CH orbital. With the observed values for a^{ax} and a^{eq} thus determined, the dihedral angle can be obtained to be $\theta\simeq 7°$. The B-value estimated here ($\rho_S=0.2195$) is 29.4 G, which shows a good agreement with the value previously estimated for the related sulfur containing a π-radical ($B=36.8$ G).[6]

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