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ESR and Structure of Cation Radicals of 2,3,6,7-Tetrahydro-1,4,5,8-tetrathiaanthracene and 2,3,6,7-Tetrahydro-1,4,5,8-tetrathiaphenanthrene

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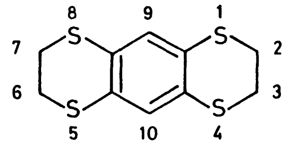
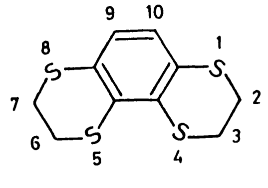
The cation radicals of 2,3,6,7-tetrahydro-1,4,5,8-tetrathiaanthracene (HTA) and 2,3,6,7-tetrathia-1,4,5,8-tetrathiaphenanthrene (HTP) have been characterized by ESR spectroscopy. The remarkable alternating linewidth effects were observed in the spectra of $HTA^{+\cdot}$ and $HTP^{+\cdot}$ both in concd H_2SO_4 and in $AlCl_3/CH_3NO_2$.

Studies of aromatic compounds bearing polythiasubstituents are very important not only in sulfur chemistry[1)] but also in material science in connection with the molecular design of organometals producing superconductivity.[2)] Along this line, 2,3,6,7-tetrahydro-1,4,5,8-tetrathiaanthracene (HTA)[3)] and 2,3,6,7-tetrahydro-1,4,5,8-tetrathiaphenanthrene (HTP)[3,4)] have recently been synthesized and their electrochemical properties have been investigated. These compounds have low oxidation potential, and the generation of stable cation radicals was observed in concd sulfuric acid.[3)] Thus, HTA and HTP are expected to work as good electron donors, and the characterization of molecular and electronic structures of these cation radicals is essential to elucidate the electronic property and behavior of HTA and HTP. In this communication we report the first ESR spectra of the $HTA^{+\cdot}$ and $HTP^{+\cdot}$ cation radicals in solution and estimate their molecular structures.



HTA



HTP

An ESR spectrum (Fig. 1a) of nine lines was obtained from a purple solution of HTA dissolved in concd sulfuric acid. The nine-line spectrum with the splitting constants of 2.39 G arises from eight equivalent protons of the ethylenedithio groups. In order to observe the ESR spectra at low temperature, the $AlCl_3/CH_3NO_2$ system[5] was used to generate the cation radicals. In the temperature range from -10 °C to -40 °C, the odd-number ($M=\pm1,\pm3$) lines became broad, while the even-number ($M= 0,\pm2,\pm4$) lines became sharp and split into triplets of 0.5 G due to the coupling of the two protons of the benzene ring of $HTA^{+\bullet}$. Thus, as the temperature became low, the main lines of spectrum changed from the nonet to the quintet. The spectrum at -57 °C is shown in Fig. 1b.

The remarkable linewidth alternation[6] observed in the $HTA^{+\bullet}$ spectra can be explained as the fluctuation of the hyperfine splitting due to the exchange motion between the axial and equatorial protons of the ethylenedithio groups. From the spectrum at the room temperature, the average hyperfine splitting constant of the axial and equatorial protons can be obtained. In the low temperature range, where the exchange rate is slow, the linewidth alternation is pronounced. At the slow exchange limit, there are two possible conformers which belong to different point-groups, C_{2h} and D_2, as shown in Fig. 2. The two conformers are almost equivalent in the total energy, and the existence ratio can be assumed to be 1:1. The spectrum of Fig. 1b was identified as a sum of spectra of the C_{2h} and D_2 conformers by using the computer simulation, where the g-values of two conformers were assumed to be iden-

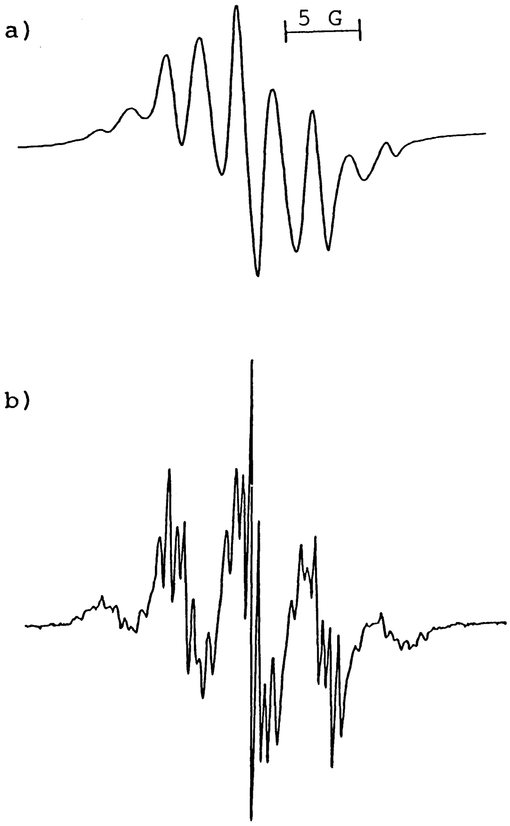


Fig. 1. ESR spectra of $HTA^{+\bullet}$ at (a) 15 °C in H_2SO_4 and (b) -57 °C in $AlCl_3/CH_3NO_2$.

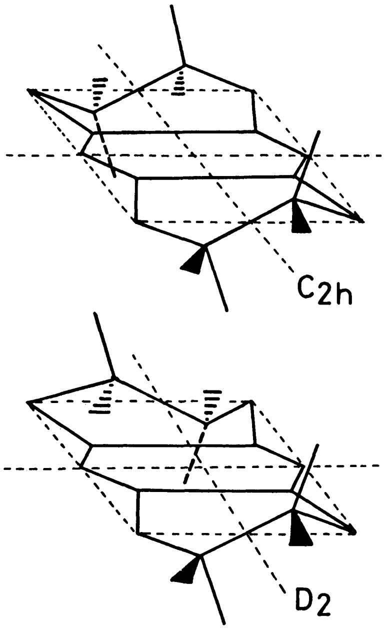


Fig. 2. Two possible conformers of $HTA^{+\bullet}$.

tical. The ESR parameters of $HTA^{+\cdot}$ are summarized in Table 1.

Also in the spectra of $HTP^{+\cdot}$, the linewidth alternation due to the axial-equatorial interconversion was observed. The spectrum in concd sulfuric acid consists of five lines of 5.37 G, and even at room temperature the linewidth alternation was observed; the center (M=0) and the outside (M=±2) lines are sharp and have the triplet substructure of 1.29 G, while the inner (M=±1) lines are broad and have no substructure. At +50 °C (Fig. 3a), the triplet substructures were observed even in the inner lines, and the further quintets with the splitting of 0.32 G newly appeared in the center and outside lines. In the low temperature range of the $AlCl_3/CH_3NO_2$ system, the inner lines were completely broaden out at -20 °C and the main quintet lines changed into the triplet whose intensity ratio is about 1:2:1. Below -40 °C, the $HTP^{+\cdot}$ spectra became more complex. The spectrum at -59 °C is shown in Fig. 3b.

Each splitting described above was identified as following. The five-main lines in the room temperature spectra arise from four β-protons on either 2,7-position or 3,6-position. The UHF MINDO/3 calculation has shown that the π-spin density on sulfur atom S_1 and S_8 is much larger than that of S_4 and S_5. Therefore, the large change of the linewidth of the main lines is due to the axial-equatorial interconver-

Table 1. Splitting constants (G) and g-values of $HTA^{+\cdot}$

Splitting constant	$AlCl_3/CH_3NO_2$ (−57 °C)		H_2SO_4 (+15 °C)
	A	B[b)]	
$a^{a}_{2,3,6,7}$ (4H)[a)]	3.93	3.81	-
$a^{e}_{2,3,6,7}$ (4H)	0.87	0.99	-
$a^{av}_{2,3,6,7}$ (8H)	-	-	2.39
$a_{9,10}$ (2H)	0.50	0.54	-
g-value	2.0082		2.0081

a) a^a, a^e, and a^{av} indicate the splitting constants of axial and equatorial and the averaged protons, respectively.

b) A and B indicate two possible conformations.

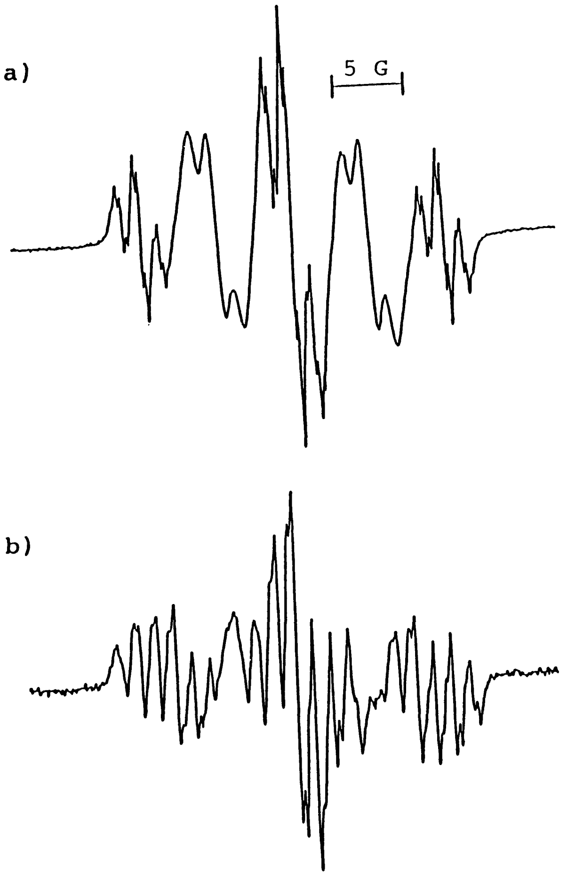


Fig. 3. ESR spectra of $HTP^{+\cdot}$ at (a) +50 °C in H_2SO_4 and (b) -59 °C in $AlCl_3/CH_3NO_2$.

sion among the four protons on 2,7-positions. The quintets of 0.32 G observed at +50 °C in the H_2SO_4 system are due to the average splitting between the axial and equatorial protons of 3,6-position. The triplets of 1.29 G observed in both H_2SO_4 and $AlCl_3/CH_3NO_2$ systems are unchanged over whole temperature range (-60 °C - +50 °C), and arise from the two protons of the benzene ring. At the slow limit, two conformers are possible for $HTP^{+\bullet}$; one belongs to C_2 group and the other C_{1h} group. The spectrum of Fig. 3b was identified as a sum of spectra of the two conformers which have g-values of the same magnitude. The ESR parameters of $HTP^{+\bullet}$ are summarized in Table 2.

Table 2. Splitting constants (G) and g-values of $HTP^{+\bullet}$

Splitting constant	$AlCl_3/CH_3NO_2$ (−59 °C)		H_2SO_4 (+50 °C)
	A	B[b]	
$a^{a}_{2,7}$ (2H)[a]	8.43	8.53	-
$a^{e}_{2,7}$ (2H)	2.52	2.42	-
$a^{av}_{2,7}$ (4H)	-	-	5.37
$a^{a}_{3,6}$ (2H)	0.39	0.40	-
$a^{e}_{3,6}$ (2H)	0.11	0.10	-
$a^{av}_{3,6}$ (4H)	-	-	0.32
$a_{9,10}$ (2H)	1.28	1.33	1.29
g-value	2.0083		2.0084

a,b) See notes of Table 1.

Dynamic properties of $HTA^{+\bullet}$ and $HTP^{+\bullet}$ can be clarified quantitatively by using the modified Bloch equations.[6)] The analysis using the computer simulation based on the modified Bloch equations is in progress.

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