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ELECTRON SPIN RESONANCE OF THIAHETEROHELICENE RADICAL ANIONS

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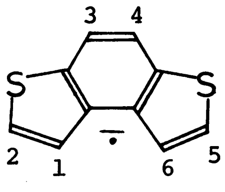
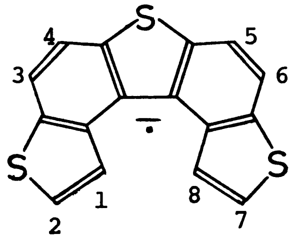
Hyperfine couplings in radical anions of benzodithiophene, [5]-thiaheterohelicene, and [7]-thiaheterohelicene were assigned by using their deuteriated compounds. The couplings calculated by a simple π-MO method agreed with the experimental ones, indicating an overwhelming contribution of π-conjugation to the spin distribution in the radicals, irrespective of the inherently staggered structure.

It is particularly interesting to examine the spin distribution in helicene radical anions in a view of their inherently staggered structure. However, this class of radicals studied previously have been limited only to the [6]-helicene radical anion,1) where the assignment of its hyperfine splitting constants(hfsc's) has been left uncertain. In a series of our synthetic2) and structural studies3) of thiaheterohelicenes with alternate thiophene and benzene ring, we have accomplished definite assignment of hfsc's for radical anions (I, II, and III) of three thiaheterohelicenes; benzodithiophene with a planar form, [5]-thiaheterohelicene with staggering3) terminals, and [7]-thiaheterohelicene with overlapping4) terminals. We now report that the assigned hfsc's are capable of being interpreted by a simple π-MO method.

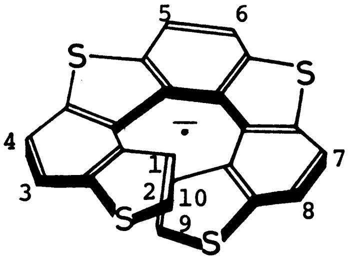
Radical anions I, II, and III were prepared under vacuum by reducing the corresponding heterohelicenes with sodium in dimethoxyethane(DME). The ESR spectra were all obtained with a well resolved pattern splitted by some sets of two equivalent protons. Hfsc's of the three radicals were unambiguously determined by generating optimal computer-simulation spectra. Figure 1 illustrates the observed and simulated spectrum of III. The availability of requisite deutero-compounds, i.e., benzodithiophene-2,5-d_2 and 3,4-d_2, [5]-thiaheterohelicene-2,7-d_2, 3-d_1, and



I



II



III

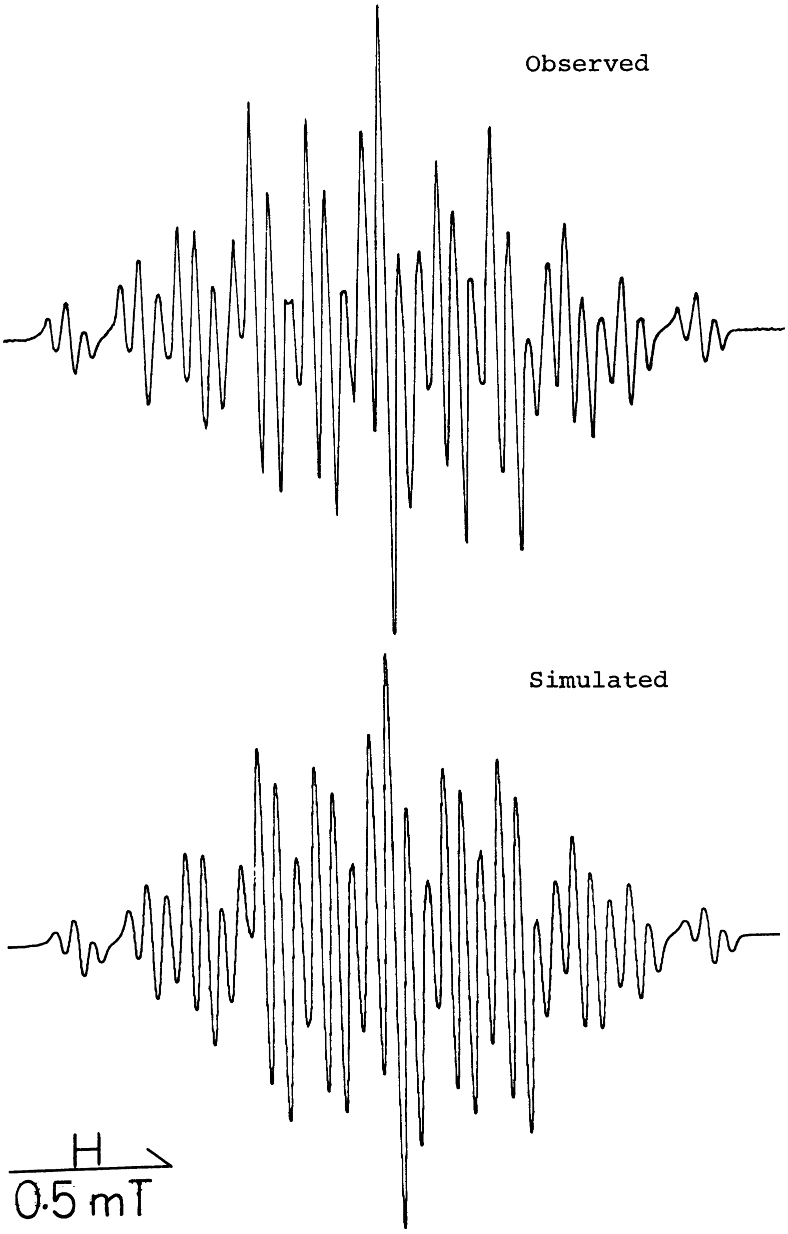


Figure 1

The ESR spectrum of [7]-heterohelicene radical anion in DME at -70°C.

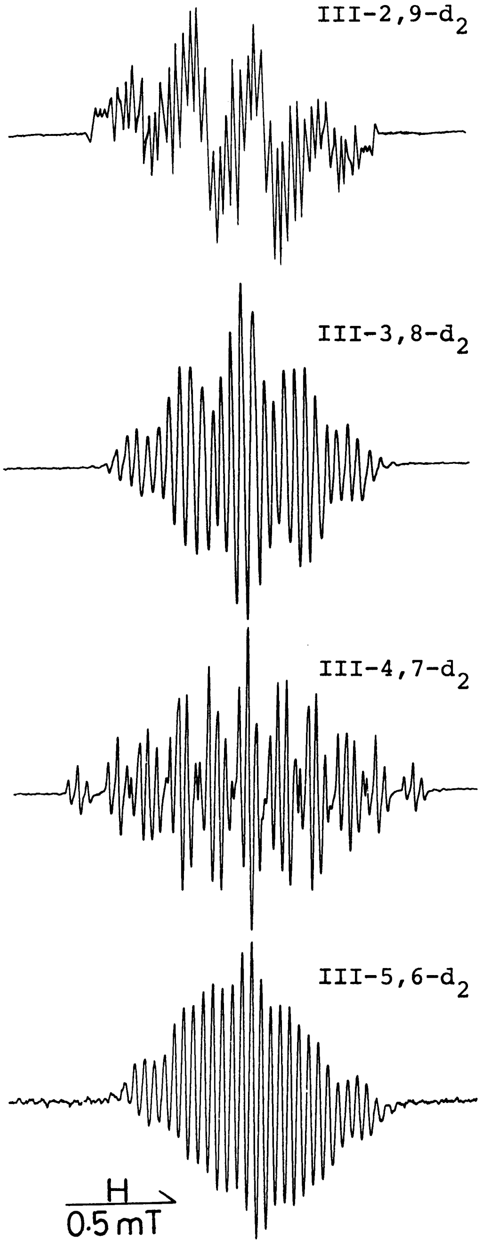


Figure 2

The ESR spectra of deutero-[7]-heterohelicene radical anions.

4-d_1, and [7]-thiaheterohelicene-2,9-d_2, 3,8-d_2, 4,7-d_2, and 5,6-d_2 established the assignment of hfsc's of the three radical anions to their ring protons. Figure 2 exemplifies ESR spectra of deutero-[7]-thiaheterohelicene radical anions. The spectra of deuteriated radical anions agreed with the spectra calculated by using the deuterium coupling $a_D[=(g_D/g_H)a_H]$ instead of the proton coupling a_H which was assumed to vanish. Hfsc's(a_{exptl}) assigned by the above procedure are listed in Table 1.

Table 1

Spin Densities and Hyperfine Coupling Constants(mT) of I, II, and III

Radical	Proton	$\lvert a_{exptl}\rvert^{a}$	ρ_{calcd}	a_{calcd}	ρ'_{calcd}	a'_{calcd}
I	1,6	0.028	-0.018	0.045		
	2,5	0.507	0.208	-0.520		
	3,4	0.417	0.168	-0.420		
II	1,8	0.051	-0.015	0.038		
	2,7	0.293	0.122	-0.305		
	3,6	0.473	0.160	-0.400		
	4,5	0.107	0.050	-0.125		
III	1,10	0.039	-0.012	0.030	-0.015	0.038
	2,9	0.180	0.077	-0.193	0.065	-0.163
	3,8	0.327	0.117	-0.293	0.123	-0.308
	4,7	$<0.02^{b}$	0.019	-0.048	0.012	-0.030
	5,6	0.287	0.094	-0.235	0.104	-0.260

[a] Determined in DME at -70°C. [b] Unresolved.

Molecular orbital calculations of spin density(ρ) in the radical anions were performed by McLachlan method[5)] using the "p" model of sulfur and polarizability correction factor $\lambda=1.2$. Integral parameters[6)] adopted for sulfur and its adjacent carbon were $\alpha_S=\alpha+0.4\beta$, $\alpha_C=\alpha+0.2\beta$, and $\alpha_{SC}=0.7\beta$. The spin densities(ρ_{calcd}), together with the coupling constants(a_{calcd}) derived from a McConnell relation[7)] $a=Q\rho$ with the Q value of -2.5 mT, are given also in Table 1. As found in the table, the calculated coupling constants reproduced well the experimental ones in the distribution and general magnitude of the coupling. Especially, it should be noted that the assignment is not insufficient even in radical anions of the staggered [5]-thiaheterohelicene and also of the overlapped [7]-thiaheterohelicene. This result suggests that the π-conjugation without σ-π mixing determines mainly the spin distribution in these radicals.

To evaluate an influence of transannular interaction, if it could exist, we searched a spin distribution most fitted to the experimental one by introducing the resonance integral β_t as a small variable between the carbons 1 and 10 and between 2 and 9 in the overlapped terminal thiophene rings of III. The best fitted spin densities(ρ'_{calcd}) and coupling constants(a'_{calcd}) were found for β_t=0.2β, as shown in the table. Certainly, the fitness seems to be ameliorated against the a_{calcd}. However, the amelioration could not be so significantly argued under approximation in McLachlan method, rather at present time, so we should remain to infer that a weak transannular interaction may possibly exist.[8)]

Therefore we conclude that the helicene radical anions behave substantially as if it were in a planar form for their spin distribution, irrespective of their staggered and/or overlapped configuration, in an accordance with an inference from Hückel[9)] and INDO calculation[10)] on π-ionization potentials and π-transition energies of neutral helicenes. Anyhow, the above unexpected result is the first finding about the spin distribution of non-planar helicene radical anions, though an investigation for radical anions which have more advanced helical structure is left to pursue.

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