

Figure 3. The esr (a) and simulated (b) spectra of the radical cation from 3,3'-dideuteriomethyl-2,2'-azinodibenzothiazole in acetone at 22°.

state organic photovoltaic cells (5).

The unpaired electron distribution was first determined by use of esr technique in many carbocyanines by Huenig *et al.* (6), who compared these results with those calculated by some MO treatments. Two of the azaviolenes were also investigated. However, it was difficult to analyze the esr spectra although one of them showed well-resolved hyperfine structure. In this study, methyl, ethyl and deuteriomethyl derivatives of the azodibenzothiazole were prepared and oxidized, all yielding stable radical cations with a counteranion, the boron tetrafluoride anion. The well-resolved esr spectra were analyzed consistently and the unpaired electron distributions were compared with those of the violene compounds as well as those obtained from the MO calculations.

The observed esr spectra taken in acetone at 22° are shown in Figures 2, 3, and 4. All of them consist of well-resolved hyperfine groups and components, which enabled us to determine electron spin distributions on the azaviolene molecules. Deuteriomethyl derivatives were employed

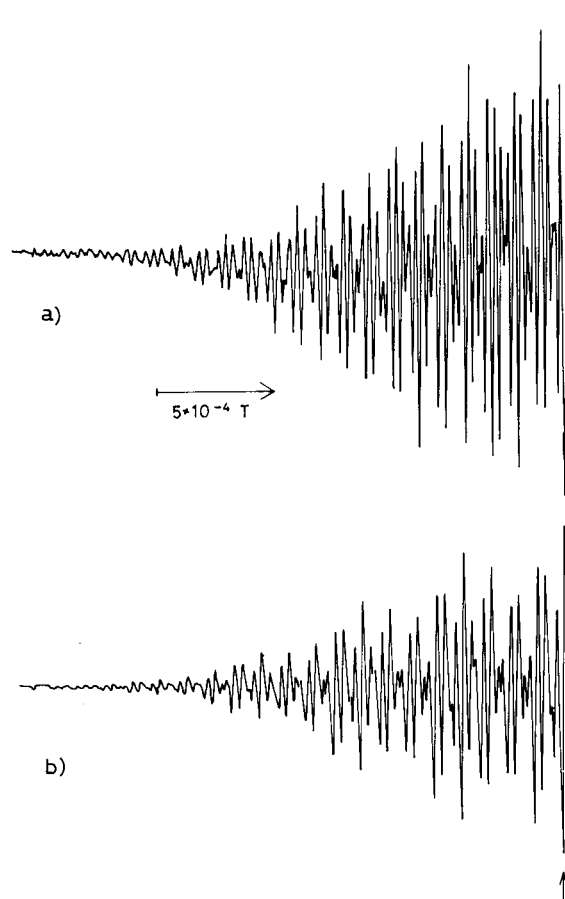


Figure 4. The esr (a) and simulated (b) spectra of the radical cation from 3,3'-dimethyl-2,2'-azinodibenzothiazole in acetone at 22°.

in order to simplify the esr spectra which include contributions from the methyl and ethyl protons to the hyperfine structure and therefore, to support the analyses of methyl and ethyl derivatives. The hyperfine splitting of a deuteron is much smaller than that of a proton because of its small magnetic moment as compared with that of a proton. Thus, the esr spectrum of the methyl derivative (Figure 4) changed to a much simpler and more well-resolved structure by the deuteron substitution as is shown in Figure 3.

The esr spectra of ethyl and deuteriomethyl compounds comprise 9 groups, which come from the largest hyperfine coupling. This characteristic is obscured by the methyl hyperfine splitting. The largest coupling of about 4 gauss (1 gauss is 10^{-4} T in SI unit) is not caused by any protons on the benzene rings of the benzothiazole groups, which have a hyperfine coupling constant of, at most, 1 gauss according to the MO calculations described later. Thus, this fact indicates that the nine groups in the deuteriomethyl

compound are due to the hyperfine interaction between the unpaired electron and the four nitrogen atoms. The similarity of the hyperfine structure in the ethyl derivative compound to that in the deuteriomethyl compound would also lead to the following conclusions; 1) the nine groups in the ethyl compound are attributable to the four nitrogen atoms and 2) the ethyl groups attached to the nitrogen atoms on which the electron spin density is the largest contribute only to the sub-structure in each of the nine groups. Presumably the latter fact could also be applied to the methyl derivative. In the computer simulation we assumed the methyl hyperfine coupling constants are in the order of magnitude of the methylene protons of the ethyl groups.

The four nitrogen atoms in each molecule are divided into two equivalent nitrogen atoms by symmetry consideration, that is, azine and ring nitrogen atoms. However, the framework of the hyperfine structure in the ethyl and deuteriomethyl compounds could be explained only by assuming four equivalent nitrogen atoms in the analysis of the esr spectra. This is also supported by the computer simulation in which intensity ratios are compared with the observed one.

All of these fundamental clues mentioned above were taken into consideration in the computer simulation of the spectra. It is supposed that the characteristics found in the ethyl and deuteriomethyl compounds are also applicable to the analysis of the methyl derivative. The results are shown in Figures 2, 3, and 4 and the coupling constants are summarized in Table I.

Table I

Experimental and Theoretical Hyperfine Coupling Constants in Gauss and Their Assignment

Assignment	Ethyl	Methyl	Deuterio-methyl	MO Calculation
N ₁	4.09	4.09	3.98	4.24
N ₂	4.09	4.09	3.98	4.20
CH ₃ ,CH ₂	0.82	1.14	— (a)	—
H ₃	0.77	0.85	0.87	1.13
H ₅	0.73	0.78	0.82	1.05
H ₄	0.35	— (b)	0.42	0.42
H ₆	0.35	— (b)	0.42	0.40

(a) Value less than the linewidth. (b) Not determined (see text).

The results indicate that a considerable amount of the unpaired electron distributes itself around the azaviolenes group, $>N-CX=N-N=CX-N<$. The next largest coupling constants come from the methyl groups which are attached to the ring nitrogen atoms. This is also true in the ethyl compound in which methylene protons in the ethyl groups show the second largest splitting. The deuterium coupling constant, A_D , seems to be obscured

within the linewidth of each well-resolved absorption line. This is compatible with the methyl hyperfine coupling constant $A_{CH_3} = 1.14$ gauss because, if one assumes the same order of magnitude of the spin density distributions in the methyl and deuteriomethyl compounds, A_D is presumed to be 0.175 gauss according to the relation $A_D/A_H = (\mu_D/I_D)/(\mu_H/I_H) \cong 1/6.5$ (7). Here μ and I are the magnetic moment and nuclear spin of deuterium (D) or proton (H), respectively. The final assignment in the small coupling constants was made by taking into account the small difference in the spin density distribution on the carbon atoms obtained from the MO calculations.

The MO calculations were made from the π -electron system of the azobenzothiazole framework by Hückel calculations, from which a spin correlation was considered by the McLachlan method (8). First the MO parameters which were used in violenes and azaviolenes by Huenig *et al.* were adopted; that is, the Coulomb integral $\alpha_N = \alpha + \beta$ for the nitrogen atom and the resonance integral $\beta_{CN} = \beta$ for the carbon-nitrogen bond. For the sulfur atom we set Coulomb and resonance integrals as $\alpha_S = \alpha + \beta$ and $\beta_{CS} = 0.5\beta$. Thus, McLachlan calculation predicts different

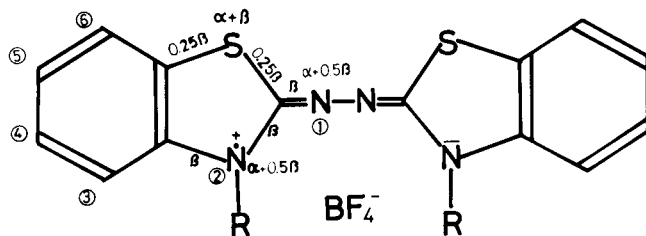


Figure 5. The optimized parameters used in the MO calculation. The Coulomb and resonance integrals for the carbon atoms are equal to α and β , respectively. The circled number indicates the nuclear species which can contribute to the esr absorption lines. This number is used in the assignment listed in Table I. $R = C_2H_5^-, CH_3^-$ and CD_3^- .

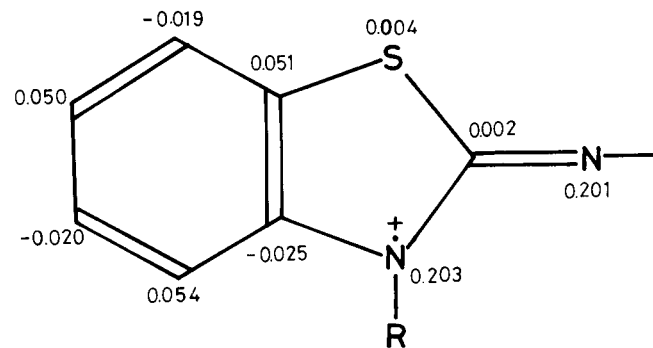


Figure 6. Spin density distribution calculated from McLachlan's method using the parameters listed in Figure 5.

spin densities on the two groups of equivalent nitrogen atoms. Therefore, we changed the parameters little by little and optimized them in order to obtain equivalent spin density distribution of all of the nitrogen atoms. The reasonable parameters determined are shown in Figure 5 and the spin density distributions in this case are summarized in Figure 6. The coupling constants predicted in this way are also listed in Table I, where we assumed McConnell's relation (9) between coupling constant and spin density with proportionality constants, $Q_C = 21.0$ gauss for the proton and $Q_N = 20.9$ gauss for the nitrogen atom. In the estimate of the nitrogen hyperfine coupling constant the effect of spin density on the adjacent carbon atoms is neglected.

The equivalent nitrogen hyperfine coupling constants are obtained by a small change in Coulomb and resonance integrals. This modification means a delocalization of the spin density from the azine nitrogen to the ring nitrogen atoms, which might cause the stability of the cation radical salt. It is noted here concerning the modification of the resonance integral between the carbon and the sulfur atoms that a decrease in resonance integral means less overlapping between these two atoms, which is supported by a molecular structure analysis carried out in some benzothiazole compounds (10). A little deformed molecular structure gives rise to a small bond angle, which may be the reason why the C—S resonance integral is reduced from 0.5β to 0.25β .

The nitrogen hyperfine coupling constants are quite similar values to those of carbon-bridged violenes (6). However, although Huenig *et al.* (6) could not simulate the observed esr spectra of two azaviolenes, they predicted the nitrogen hyperfine coupling ratio $A_{N_1}/A_{N_2} \cong 1.4$. In this investigation the equal amount of delocalization of the unpaired electron on two types of nitrogen atoms is unambiguously shown by the esr simulation in the azaviolenes including a deuterated compound. The proton coupling constants on the benzene rings are found to be a little smaller than those predicted by McLachlan's calculation. However, they are relatively in good agreement with the theory, especially the data indicating a slight difference between A_{H_3} and A_{H_5} , just the same as the estimated one.

It should be pointed out finally that the analysis of the esr spectrum of the methyl derivative (Figure 4) is not necessarily a final one, because we could not find a reasonable set of hyperfine coupling constants in the H_4 and H_6 positions by the computer simulation (see Table I). These values would be expected to be a little less than half of A_{H_3} and A_{H_5} , judging from the hyperfine coupling constants for the ethyl and deuteriomethyl derivatives and also from the theoretical calculations. The simulated spectrum in Figure 4 shows a little disagreement with the observed spectrum, because it is recorded on the basis of a set of

hyperfine coupling constants of the nitrogen atoms and the methyl, H_3 , and H_5 protons.

EXPERIMENTAL

Measurement.

The esr spectra were observed by means of an X-band esr spectrometer (JEOL ME3) with 100 KHz field modulation at room temperature. The magnetic field was calibrated by the hyperfine splitting of ^{14}N of peroxyamine disulfonate ion. The spectral simulations were carried out with a JEOL spectral computer (model JEC-6). The molecular orbital calculations were made both with a micro-computer (Sharp MZ-80) and with a FACOM M-190 computer at the Data Processing Center, Kyoto University. Acetonitrile, ethyl alcohol and acetone were used as solvents for the esr measurements after being thoroughly dried and degassed. It was found that acetone is the best solvent to observe well-resolved esr spectra.

Some of the preparation processes were already reported in the literature (11-14), but some devices were adopted for high yields especially in the early stages of the preparation processes.

2-Ethylthio-3-ethylbenzothiazolium Iodide (Quaternary Salt).

2-Ethylthiobenzothiazole was prepared by Kucherov (11) and Brooker *et al.* (12) and the formation of quaternary salts from 2-methyl and 2-ethylbenzothiazole was reported (13). These yields, however, were found to be very poor. Accordingly, the reaction was made in a sealed glass tube, giving an excellent high yield.

The well-dried sodium salt of mercaptobenzothiazole (5.2 g) was dissolved in a glass tube with 20 ml of ethyl alcohol. After adding ethyl iodide (4.68 g) on an ice bath, the glass tube was sealed off immediately and then heated to 100° on a hot water bath for 15-20 hours. Ethyl alcohol was evaporated under reduced pressure after opening the reaction tube. The product (2-ethylthiobenzothiazole) was extracted with ethyl ether. After removal of ethyl ether from the extract by evaporation under reduced pressure, a little excess of ethyl iodide (5.5 g) was added at ice temperature. This time no solvent was necessary. The reaction tube was again sealed off and heated to 100° for 15-20 hours. Ethyl iodide was removed by evaporation, yielding the quaternary salt which easily decomposes.

The methyl derivative of the quaternary salt was prepared by almost the same method as above except the heating temperature, $45-55^\circ$. Moreover, the reaction tube has two chambers in order to be able to mix methyl iodide after it is sealed off. This is because the methyl iodide would start to react with the sodium salt of mercaptobenzothiazole or 2-methylthiobenzothiazole even at ice temperature.

3,3'-Diethyl-2,2'-azinodibenzothiazole.

3,3'-Diethyl-2,2'-azinodibenzothiazole was synthesized according to the method of Huenig *et al.* (13). The quaternary salt (7.1 g) was dissolved in 16 ml of ethyl alcohol and then hydrazine (0.5 ml) was added. After the generation of the mercaptan, triethylamine (2.8 ml) was added dropwise, then the solution was kept cool in an ice bath. The precipitate was dried and recrystallized from glycolmonomethyl ether, mp $204-208^\circ$ (lit $193-202^\circ$).

Radical Salt of 3,3'-Diethyl-2,2'-azinodibenzothiazole.

This synthetic method was also reported by Huenig *et al.* (13). 3,3'-Diethyl-2,2'-azinodibenzothiazole (1.77 g) was dissolved in 50 ml of DMF, then lead(IV) acetate (2.2 g) with a little amount of acetic acid was added under stirring. Into the dark blue solution sodium tetrafluoroborate (1.65 g) with 18 ml DMF was mixed dropwise. The blue needles were precipitated by cooling to 0° , mp $186-190^\circ$ (lit mp $186-190^\circ$).

The radical salts and their precursors of the methyl and deuteriomethyl derivatives were synthesized by the same method described above.

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