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ENDOR Study of Benzothiazolone Azine Cation Radicals by Means of a TM_{110} Mode Cavity

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The electron nuclear double resonance (ENDOR) spectra of benzothiazolone azine cation radicals were observed by means of an ENDOR spectrometer equipped with a TM_{110} mode cavity. Highly diluted solutions of the radicals and a high radiofrequency power of 300 W facilitated the ENDOR observation. The obtained ENDOR values are different from the previously published results determined only from the ESR data, especially for the substituted alkyl groups. The assignment of the hyperfine coupling constants was made on the basis of the molecular orbital calculations as well as the re-examination of the ESR spectrum simulation. Good agreement between the calculated and the measured spectra is obtained if one assumes that the hyperfine coupling constants of the two different sets of nitrogen nuclei are equal as has been pointed out earlier.

Benzothiazolone azine and similar systems are well-known as two-step redox systems.[1] One can see easily from Fig. 1 that the intermediate compound B is a radical species. Hünig *et al.*[2] tried to observe ESR spectra of the benzothiazolone azine cation radicals, but no well-resolved ESR spectra could be obtained. As far as we know, no further ESR experiments have been performed to obtain more knowledge about spin density distributions in these systems. Recently well-resolved ESR spectra were obtained by means of a cylindrical TE_{011} mode cavity and spectral simulations were carried out.[3] No ENDOR spectra, however, could be observed successfully with the same type of ENDOR cavity. The nitrogen nucleus causes a short relaxation time due to the quadrupole moment. It is, therefore, very difficult to saturate the ESR transition of the radical containing the nitrogen nucleus although this is needed for performing ENDOR spectroscopy.

Möbius *et al.*[4] developed a TM_{110} mode cavity several years ago. The TM_{110} mode cavity allows one to apply higher radiofrequency power than the TE_{011} mode cavity does. In addition, the direction of the magnetic field of the radiofrequency is the same as that of the sample tube. The TM_{110} mode cavity, therefore, is more appropriate for the application of the ENDOR spectroscopy to systems which become saturated only with difficulty, like benzothiazolone azine cation radicals. This advantage was utilized for ^{14}N ENDOR observation of di-*t*-butyl nitroxide, which is not saturated easily, presumably because of a quadrupole moment and high freedom of molecular motions.[5]

The assignment and analysis of the coupling constants and ESR spectra in the work published previously[3] were mainly performed by means of MO calculations: Hückel and McLachlan method.[6,7] As is mentioned in that work, the obtained results are not necessarily final and conclusive ones. Successful application of ENDOR spectroscopy can help to confirm the calculated data and the conclusions in the published work.

Experimental

The synthesis of 2(3-alkyl)-benzothiazolone azine is described elsewhere.[1,3] The cation radicals of $\mathbf{1}^{\dot{+}}$, $\mathbf{2}^{\dot{+}}$, and $\mathbf{3}^{\dot{+}}$ (Fig. 2) can be obtained by oxidation of the neutral compound with lead tetraacetate in various kinds of solvents. In our case, the oxidation of the neutral precursor was performed in an evacuated sealed sample tube using dichloromethane as a solvent. The previously published ESR spectra were observed in acetone at 295 K. Acetone was found to be inappropriate for ENDOR observation since it has a higher polarity than dichloromethane. Polar solvents can be disadvantageous for the ENDOR spectroscopy, since they cause lower *Q*-values for the cavity.

The ESR spectra of $\mathbf{1}^{\dot{+}}$, $\mathbf{2}^{\dot{+}}$, and $\mathbf{3}^{\dot{+}}$ were recorded with a JEOL ES-EDX2, FE 3X spectrometer equipped with a cylindrical TE_{011} mode cavity. The observed ESR spectra show an observable temperature dependence, which is probably caused by the molecular motions of the benzothiazolone groups with respect to the inter-nitrogen bond as well as those of methyl and ethyl groups attached to the nitrogen atoms. The anisotropic effects of the nitrogen and the sulfur atoms may also be responsible. The ESR spectrum of $\mathbf{1}^{\dot{+}}$ is not perfectly symmetric around the center. This is also attributed to the molecular motions and the anisotropic effects. The displayed ESR spectra in Figs. 3—5 were observed in an extremely diluted acetone solution

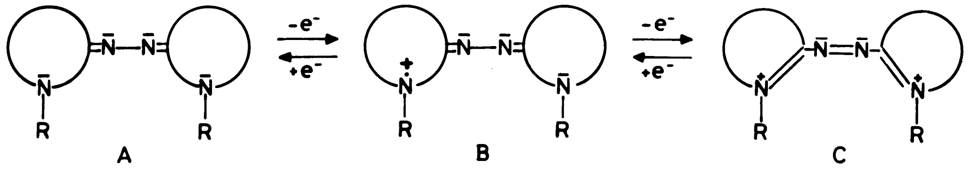

Fig. 1. A two-step redox system. The three oxidation levels are called reduced from (A), semiquinone (B), and oxidized form (C).

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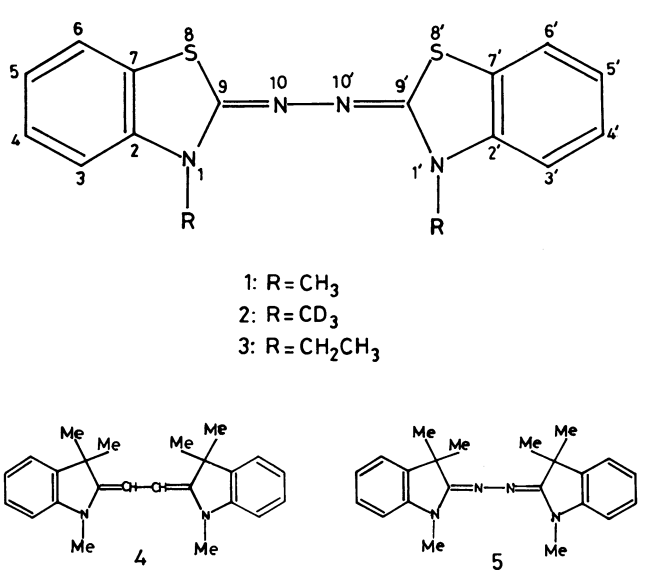

Fig. 2. The molecular structures **1**, **2**, and **3** studied in this work and similar systems **4** and **5**.

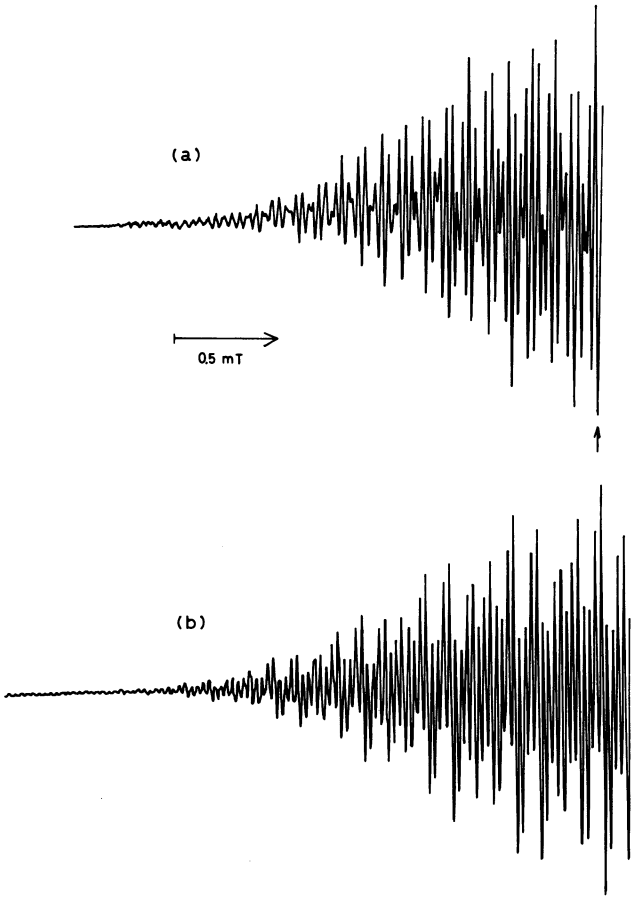

Fig. 3. The ESR and the simulated spectra of **1**$^{+}$. The ESR spectrum (a) is recorded in acetone at 295 K.

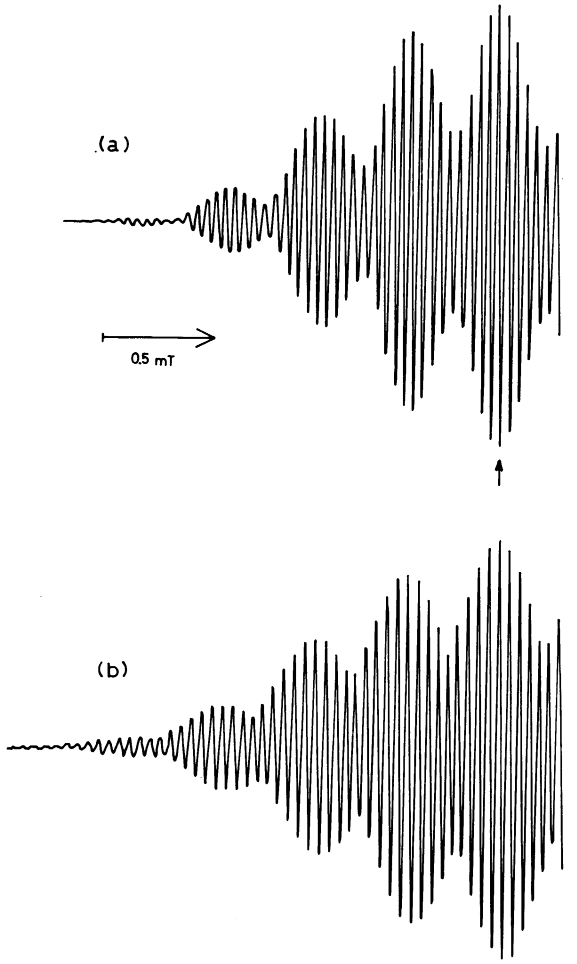

Fig. 4. The ESR and the simulated spectra of **2**$^{+}$. The ESR spectrum (a) is recorded in acetone at 295 K.

of the corresponding cation radicals, which had been isolated and purified several times. The ESR spectra when ENDOR was observed were rather less resolved because the oxidation reaction was performed in the sample tube under high vacuum and because ESR observation was made with an 80 Hz field modulation in a cylindrical TM_{110} mode cavity. Good agreement of the calculated and the original spectra were obtained for **1**$^{+}$, **2**$^{+}$, and **3**$^{+}$ on the basis of the MO data and the hyperfine coupling constans determined from the ENDOR, as is shown in Figs. 3—5. The hyperfine coupling constants were calibrated by using an alkaline solution of a nitrosyl bis(sulfate) ion. The original ESR spectra were recorded with a 100 kHz field modulation in acetone at 295 K, whereas in ENDOR an 80 Hz field modulation was employed.

The ENDOR spectra (Fig. 6) were observed by means of the TM_{110} mode cavity under the following conditions: microwave power 50 mW, radiofrequency power 300 W (ENI-type A300 power amplifier), field modulation 80 Hz, modulation amplitude 0.1 mT, and FM modulation of radiofrequency 2.5 kHz. For the ENDOR spectroscopy, a more diluted (nearly colorless) solution than that for the ESR spectroscopy had to be used. No ENDOR spectra could be obtained in the same concentration which produced the best ESR. The best ENDOR spectra were observed at 223 K. In Table 1 the hyperfine coupling constants of **1**$^{+}$,**2**$^{+}$, and **3**$^{+}$ are listed.

Discussion

One can see from the ENDOR values in Table 1 that the hyperfine coupling constants of **1**$^{+}$, **2**$^{+}$, and **3**$^{+}$

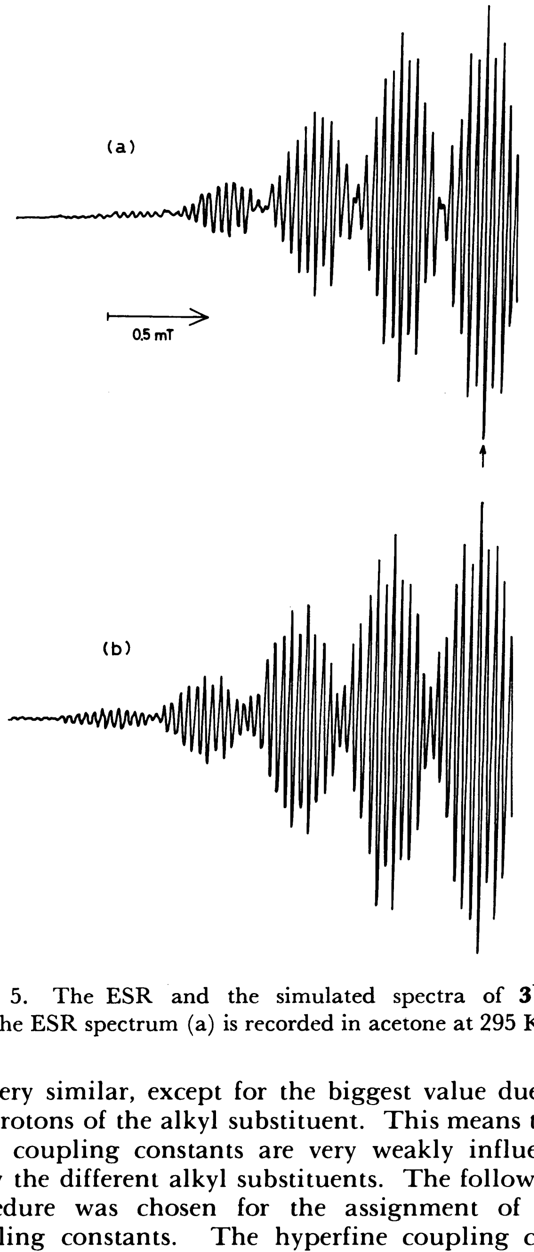

Fig. 5. The ESR and the simulated spectra of **3**$^{\dot{+}}$. The ESR spectrum (a) is recorded in acetone at 295 K.

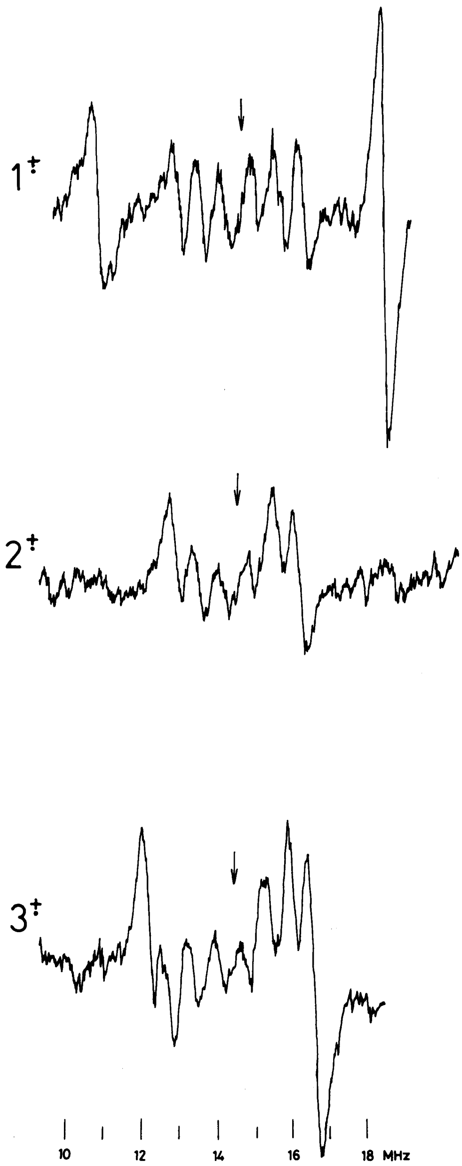

Fig. 6. The ENDOR spectra obtained in dichloromethane at 223 K. The arrow indicates the free proton frequency.

are very similar, except for the biggest value due to the protons of the alkyl substituent. This means that these coupling constants are very weakly influenced by the different alkyl substituents. The following procedure was chosen for the assignment of the coupling constants. The hyperfine coupling constants of the methyl protons in **1**$^{\dot{+}}$ can be easily assigned, since the ENDOR signals in the spectrum of **1**$^{\dot{+}}$ at 10.63 and 18.18 MHz disappear in the spectrum of **2**$^{\dot{+}}$. These signals also do not appear in the spectrum of **3**$^{\dot{+}}$ in which another pair of absorption lines appears instead. Thus, the biggest proton coupling constants 0.268 and 0.154 mT can be assigned to the methyl protons and the methylene protons of the ethyl groups, respectively. Then, the remanining coupling constants must be assigned to the ring protons of the two benzo moieties. There are four different sets of the ring protons, but the recorded ENDOR spectra for all systems show only three different values for the ring protons. One can, therefore, conclude either that the missing coupling constant must be less than the line width (*ca.* 0.015 mT) or that two coupling constants have similar values so that their absorption lines are not resolved. The best calculated spectra are obtained if one assumes that the missing coupling constant is almost the same as the smallest of the three. Hückel and McLachlan methods for the calculation of spin density, as is discussed later, predict the same conclusion. This is also compatible with the ESR simulation. Thus, the smallest coupling may be assigned to two kinds of equivalent protons, so that one has three different sets of the ring protons out of four equivalent proton groups.

The assignment of the coupling constants to the ring protons was made on the basis of the MO data obtained from the Hückel and McLachlan methods. The π-electron MO calculation of benzothiazolone azine framework was discussed in detail in the previous paper.[3] We employed the same MO parameters and no further modification was made. The results are shown in Table 1, where the proton hyperfine coupling constants are also estimated using the

TABLE 1. HYPERFINE COUPLING CONSTANTS AND MO RESULTS FOR THE RADICALS $\mathbf{1}^{+\cdot}$, $\mathbf{2}^{+\cdot}$, and $\mathbf{3}^{+\cdot}$ IN 10^{-4} T UNITS

Radical		$\mathbf{1}^{+\cdot}$		$\mathbf{2}^{+\cdot}$		$\mathbf{3}^{+\cdot}$		McLachlan	
Position		ESR	ENDOR	ESR	ENDOR	ESR	ENDOR	Spin density	Coupling constant
1,1′	(2N)[a]	4.09	—	3.91	—	4.09	—	0.2025	—
10,10′	(2N)	4.09	—	3.91	—	4.09	—	0.2006	—
3,3′	(2H)	1.12	1.14	1.34	1.14	1.19	1.19	0.0540	1.13
4,4′	(2H)	0.33_5	0.29	0.43_5	0.26	0.40	0.24	−0.0201	0.42
5,5′	(2H)	0.86_5	0.74	0.87	0.74	0.80	0.74	0.0502	1.05
6,6′	(2H)	0.33_5	0.29	0.43_5	0.26	0.40	0.24	−0.0194	0.40
$R=CH_3$	(6H)	2.97	2.68	—	—	—	—	—	—
$R=CD_3$	(6D)	—	—	0.43_5	—	—	—	—	—
$R=CH_2$[b]	(4H)	—	—	—	—	1.58	1.54	—	—

a) Number of the equivalent nuclei, N, H, or D. b) Methylene protons of the ethyl group, $R=CH_2CH_3$.

McConnell equation[8] with a proportionality constant $|Q|=2.1$ mT. By comparing the ENDOR results with those arrived at previously from the ESR study,[3] the following conspicuous facts are revealed: 1) the alkyl protons have much larger coupling constants (almost two times bigger) than those from the ESR data[3]; 2) ENDOR shows slightly bigger coupling constants of the ortho protons ($H_{3,3'}$) of the two benzo moieties and slightly smaller ones of the two meta protons ($H_{4,4'}$ and $H_{6,6'}$), while in the para protons ($H_{5,5'}$) the constants have almost the same value; 3) in conjunction with fact 1), one has to take into account the deuteron hyperfine coupling constant, which was neglected in the previous work.[3] After we consider the reliability of proton ENDOR, we re-examined the spectral simulation of the ESR on the basis of the coupling constants determined from the ENDOR. First, the big nitrogen hyperfine coupling constants are again confirmed: these constitute the fundamental group pattern of the ESR spectra, as is discussed in the literature.[3] Next, by changing the proton coupling constants little by little from the ENDOR values, as well as changing the deuteron coupling constant starting from 0.041 mT predicted from $A_D/A_H=1/6.51437$[9] where $A_H=0.268$ mT of the methyl protons, an acceptable set of the hyperfine coupling constants for each compound is obtained; these are shown in Table 1. Figures 3—5 are comparisons between the experimental and the simulated spectra. The newly determined values do not deviate from the ENDOR values as much as 0.03 mT. Such agreement is rather satisfactory, considering the fact that the ESR spectra were recorded under different conditions (*e.g.* different temperature and solvent) for the best resolution.

The ESR simulations in this paper are more reliable than the previous ones, because the ENDOR results are taken into account this time. Again, the equivalent hyperfine coupling constants could be assigned to the thiazolone and the bridged nitrogen atoms. This may support the validity of the choice of the MO parameters in the previous paper.[3] Agreement between the experimental and the theoretical proton hyperfine coupling constants at the ring positions are also excellent, except for the para positions ($H_{5,5'}$). The McLachlan calculation predicts a quite small difference between the ortho ($H_{3,3'}$) and para ($H_{5,5'}$) protons. The deuteron coupling constants is taken into consideration this time and found to be 0.0435 mT, giving $A_D/A_H=1/6.8$. From the methyl coupling constant 0.298 mT, 0.0456 mT is expected theoretically.[9]

Next, we comment about the R-substitution effect. The alkyl substitution never has a severe effect on the unpaired electron distribution, as was said in the first section of this discussion. However, the spectrum itself is influenced dramatically because of the big spin density at the nitrogen atoms to which the alkyl groups are attached. There are a lot of data for the nitrogen and the methyl or ethyl proton hyperfine coupling constants where the alkyl groups are attached directly to the nitrogen atom.[10—12] For the nitrogen and methyl protons, the same order of magnitude of the couplings are commonly observed.[12] In this work, however, the methyl hyperfine coupling constant is reduced to 75%, as compared to the nitrogen value. This may be caused by the deformed bond angle around the nitrogen atom in the thiazolone ring. On the other hand, the relation in magnitude between the methyl and the ethyl coupling constants is as usual, *i.e.* the methylene protons of the ethyl have sometimes *ca.* 50% of the methyl coupling constants.[12]

Two similar systems (**4** and **5** in Fig. 2) were investigated some years ago.[2] They do not contain sulfur but non-π part, $>C(CH_3)_2$, is introduced in the sulfur position of the compounds **1**—**3**. Therefore, the π-system does not extend over the five-membered rings, as in **1**—**3**. The ESR spectrum of $\mathbf{5}^{+\cdot}$ could not be analyzed, since it showed a poor resolution. A comparison of the calculations for $\mathbf{1}^{+\cdot}$-$\mathbf{3}^{+\cdot}$ and $\mathbf{4}^{+\cdot}$-$\mathbf{5}^{+\cdot}$ shows a similar behavior. The large spin densities are greatly delocalized in the ortho and para, and less delocalized in the meta positions, both for $\mathbf{1}^{+\cdot}$, $\mathbf{2}^{+\cdot}$, $\mathbf{3}^{+\cdot}$, and for $\mathbf{4}^{+\cdot}$, $\mathbf{5}^{+\cdot}$. The Hückel and McLachlan methods give inequivalent spin densities for the two different sets of nitrogen nuclei in $\mathbf{5}^{+\cdot}$, $A_{N1}/A_{N10}=1.4$.[3] This is also the case for $\mathbf{1}^{+\cdot}$, $\mathbf{2}^{+\cdot}$, and $\mathbf{3}^{+\cdot}$ when the proposed set of the MO parameters is used. In $\mathbf{4}^{+\cdot}$ the nitrogen and the vinyl protons have the same coupling constant. This, however, does not mean that the same spin densities are located on these nuclei. The nitrogen coupling constant in $\mathbf{4}^{\dagger}$ differs only by 0.021 mT from that in $\mathbf{1}^{\dagger}$, $\mathbf{2}^{\dagger}$, $\mathbf{3}^{\dagger}$. Nevertheless, the coupling constants of the methyl protons do not have similar values. These inconsistencies certainly suggest the necessity of the ENDOR experiments in the two above-mentioned systems. A common feature of all systems ($\mathbf{1}^{\dagger}$ through $\mathbf{5}^{\dagger}$) is that about 70% of the spin density is located on the atom sequence $>\text{N}-\overset{|}{\text{C}}=\text{N}-\text{N}=\overset{|}{\text{C}}-\text{N}<$ and only a small amount is located on the two benzo moieties.

Some concluding remarks should be made about the TM_{110} mode cavity. The application of this cavity has not yet been widely extended after its development.⁴⁾ The collected experience with this cavity shows that it offers a better resolution in the ENDOR spectroscopy than the TE_{011} mode cavity and it also allows one to observe much more easily nitrogen ENDOR.⁵⁾ However, we did not succeed till now in detecting the nitrogen ENDOR for the present series of compounds. This may be due to the properties of the bobbin with which the radiofrequency signal is transmitted to the cavity.

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