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# Nuclear Magnetic Resonance Spectra of Benzoxadiazole, Benzothiadiazole, Benzoselenadiazole and Quinoxaline

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The NMR spectra of the benzenoid ring protons in benzoxadiazole, benzothiadiazole, benzoselenadiazole and quinoxaline have been analyzed as AA'BB' spin systems by an iterative method. The theoretical spectra showed good agreements with the experimental spectra in line frequencies and their relative intensities. The obtained chemical shifts and coupling constants exhibit some interesting features corresponding to the molecular structural changes arised from the replacement of oxygen by sulfur, selenium and carbon double bond. The chemical shift $\nu_0\delta_{AB}$ was found to decrease with the more delocalized $\pi$-electron distribution and to suggest a d-orbital model for sulfur. The relative magnitudes of the two *ortho*-coupling constants and their variations from molecule to molecule were tentatively correlated with the changes of the internal bond angles in the benzenoid ring. The relation of $J_{\text{para}} > J_{\text{meta}}$ in benzoxadiazole was interpreted in terms of a negative contribution of $\pi$-electrons to $J_{\text{meta}}$.

## Introduction

More experimental data on the nuclear magnetic resonance (NMR) spectra are desirable as an aid in developing an adequate theory of the proton–proton coupling in a benzene ring fused to heterocyclic ring. In this contex, a series of the compounds investigated in the present paper are interesting for several reasons. The NMR spectra of the benzenoid ring protons of these compounds are of the AA'BB' type and amenable to rigorous analysis. Furthermore, these compounds form a series of closely related molecules suitable for a study of the effect upon the NMR spectral parameters of the replacement of oxygen by sulfur, selenium, or carbon double bond.

The general analyses of AA'BB' type spectra have been discussed by a number of authors[2-6] who treated the effects of the magnitudes and relative signs of the NMR parameters in considerable details. In the present paper, the NMR spectra of the related compounds have been fully analyzed and their chemical shifts and coupling constants are compared.

### Experimental

The spectra were obtained with a high resolution spectrometer type JNM-C-60H, operating at 60 MHz. The spectrum of each sample was run several times and the arithmetic mean of a line position was used for the analysis. The tetrachloromethane solution of the compound employed here was prepared to a concentration of 10 mole per cent. In sampling, the solvent containing a few per cent of TMS was degassed thoroughly in a side tube attached to a high vacuum line by the repetitions of freezing in liquid nitrogen, pumping and thawing and then it was transferred by distillation into a NMR sample tube (5 mm o.d.) with small amounts of the compound so as to prepare a solution of the necessary concentration. The sample

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1) Location: *Oshika 160, Shizuoka.*
2) J.A. Pople, W.G. Schneider and H.J. Bernstein, *Can. J. Chem.*, **35**, 1060 (1957).
3) V.B. Dischler and G. Englert, *Zeit. für Natur.*, **16a**, 1180 (1961).
4) D.R. Whitman, *J. Chem. Phys.*, **36**, 2085 (1962).
5) D.M. Grant, R.C. Hirst and H.S. Gutowsky, *J. Chem. Phys.*, **38**, 470 (1963).
6) H.M. Hutton and T. Schaeffer, *Can. J. Chem.*, **41**, 2429 (1963).

tube was sealed under a high vacuum. Benzoxadiazole,[7] benzothiadiazole,[8] and benzoselenadiazole[9] were synthesized, quinoxaline being prepared by one of the authors.

## Analysis of Spectra

The NMR spectra of the present case can be analyzed as AA′BB′ or AA′XX′ when the chemical shift difference $\nu_0\delta_{AB}$ is enough large relative to the coupling consants involved. The complex relation between the AA′BB′ spectrum and the magnetic parameters frequently leads to the analysis being rather difficult. Because of this, several indirect methods as quoted above have been adopted, where assignments are made firstly by constructing a theoretical spectrum with an approximate AA′XX′ spin system and then by decreasing $\nu_0\delta_{AB}$ value for the modifications of the line positions. This process gives a correct assignment if the original spectrum is constructed with a set of the coupling constants not too dissimilar to the real ones. When an assignment is made, $\nu_0\delta_{AB}$ and $J$′s can be derived using adequate line intervals in the spectrum. This method, however, is useless in differentiating between $J_{AA'}$ and $J_{BB'}$ and between $J_{AB}$ and $J_{AB'}$, and involves a tedious trial-and-error procedure for obtaining the magnitude of $J_{AA'}+J_{BB'}$.

In order to make the analysis more refined and systematic, an iterative analysis method developed by Swallen and Reilly[10] has been applied to the work described here. For the convenience of later discussions a brief review of this method will be given in the following.

Firstly, after an assignment has been made (even a partial assignment may be adequate), the energy level differences are correlated with the observed transition frequencies according to the next equation, one for each transition;

$$E_i-E_j=\nu_{ij}. \quad (i=1, 2, \cdots, n-1,\ i<j)$$

$n$: the number of the energy levels.

As this set of equations have a rank of $n-1$, the next equation derived from the invariance of the trace sum should be included.

$$\sum_{i}^{\text{all}} E_i=0$$

Another equation obtained from the relation between the trace of sub-matrix is also added sometimes. For example, this in a four spin system is

$$\sum_{I_z=1} E_i+\sum_{I_z=-1} E_j=0.$$

The above equations overdetermine the energy levels and can be solved conveniently by a least-squares technique.

Once the experimental energy levels are determined, the initial values are given for the magnetic screening constant $h_i$ and spin-spin coupling constant $J_{ii}$ which are expressed in the spin Hamiltonian (H) as below;

$$H=\sum_i 2h_iI_{zi}+\sum_{i<j}\sum J_{ij}\mathbf{I}_i\cdot\mathbf{I}_j.$$

At the first stage of iteration, approximate eigenvectors derived with the initial parameters can be used to obtain improved values for the diagonal matrix elements of H by the inverse transformation

$$H_{ii}=(S\Lambda_{\text{obs}}S^{-1})_{ii}=\sum_k S_{ik}{}^2E_k,$$

where the observed $E'_i$s are expressed as a diagonal matrix $\Lambda_{\text{obs}}$. $H_{ii}$ is a set of linear equations from which better values for the parameters can be readily obtained by a least-squares technique. This process can be continued until a convergence solution of the parameters is obtained.

Finally, a theoretical spectrum is constructed with the best fitting magnetic parameters, where the relative intensity of the transition between spin states $\Psi_1$ and $\Psi_2$ can be given as $[\Psi_1S\Psi_2]^2$; $S=1$ for terms involving a pair of spin product functions differing in the spin of one nucleus alone, and is zero otherwise. The errors in the final parameters ($\delta P_m$) can be estimated from

$$\delta P_m=[\sum_i(\partial P_m/\partial E_i)^2(\delta E_i)^2]^{1/2},$$

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[7] A.G. Green and F.M. Rowe, *J. Chem. Soc.*, **1917**, 618.

[8] A.M. Khaletskii, and V. G. Pesin *Chem. Abstracts*, **46**, 106 (1952).

[9] B.P. Heinemann, *Chem. Abstracts*, **50**, 13885 (1956).

[10] J.D. Swallen and C.A. Reilly, *J. Chem. Phys.*, **37**, 21 (1962).

where $\delta E_i$ is the rms error in the experimental energy level $E_i$ and $\partial p_m/\partial E_i$ is obtained by doing one additional iteration to determine the changes produced in $P_m$ by a small variation in each of the energy levels.

Actual programmings and numerical calculations were carried out using the Tokyo University HITAC 5020 computer.

## Results and Discussion

The structural formulas of the related compounds and definitions used in designating the protons and coupling constants are shown in Fig. 1.

Fig. 2 shows the measured spectra. Each of them gives a mirror image pattern composed of the A multiplet and B multiplet though the position of the center changes relative to the internal reference signal of TMS.

Among the 28 theoretical lines of a AA′BB′ system, all except the four combination bands have measurable intensities. No long-range coupling was observed between the α-proton to nitrogen and the other protons in the spectrum of quinoxaline. The assignment of each line is given on the spectra shown in Fig. 2 according to conventional notations. A number of other assignments obtained by interchanging the origins between the lines 1 and 2 and between the lines 3 and 4 were found to give unsatisfactory results for the iterative analysis.

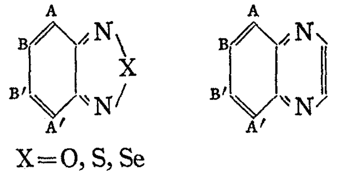

Fig. 1 The Structural Formulas of the Analyzed Compounds and the Notations used in Designating the Protons and Coupling Constants

It is impossible to assign the two multiplets to the two sets of the equivalent protons without further informations. Nevertheless, the proton A closer to the nitrogen is thought to correspond to the low-field multiplet on account of the more effect of the nitrogen magnetic

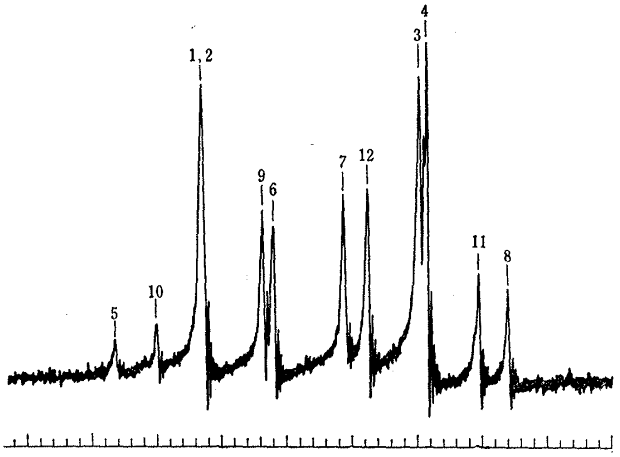

Fig. 2a. The Lower-field Part of the Benzoxadiazole Spectrum

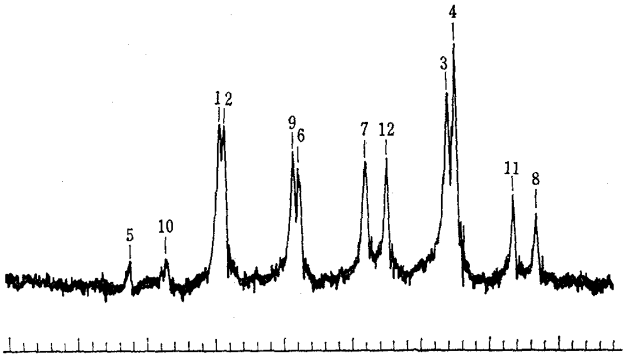

Fig. 2b. The Lower-field Part of the Benzothiadiazole Spectum

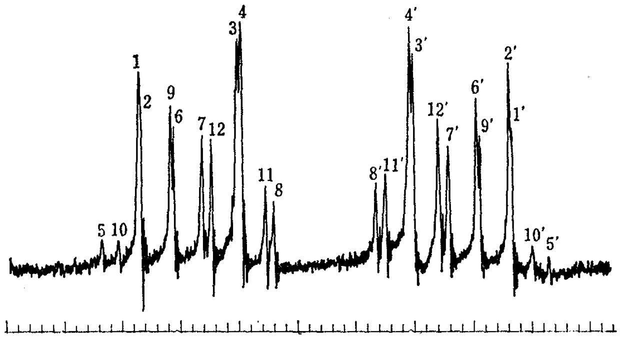

Fig. 2c. The NMR Spectrum of Benzothiadizaole

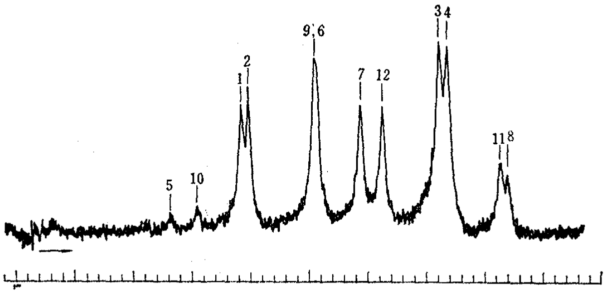

Fig. 2d. The Lower-field Part of the Quinoxaline Spectrum

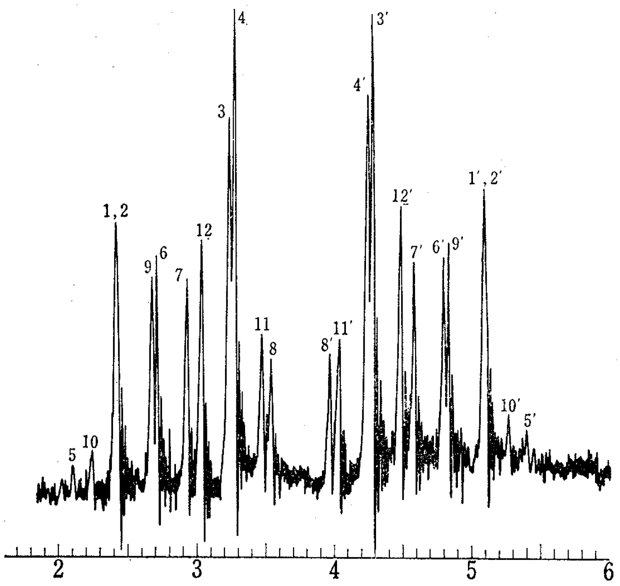

Fig. 2e. The NMR Spectrum of Benzoselenadiazole

anisotropy just as have been illustrated in many nitrogen–heterocyclic molecules. In this case, the fact that the 1 and 3 lines in the lower multiplet originating from the transition related with non-mixing spin functions are somewhat broadened (the 1 line can be resolved in the spectra of benzothiadiazole and quinoxaline alone) will be correlated with the quadrapole broadening in interaction with the nitrogen. In all of the spectra, the lines due to transitions 3 and 4 tend to overlap as do 1 and 2. In the spectra of quinoxaline, the lines 9 and 6 are overlapping though the lines 1 and 2, and the lines 3 and 4 are resolved. A AA'XX' approximation can combine this with such a change in the parameters as the decrease of $J_{AA'}$. At any rate, the spectra obtained in the present work are considerably available for the analysis by virtue of the separations of the lines 1 and 2, and of the lines 3 and 4.

As an example of the experimental energy level diagram determined by a least-squares method, that of the benzothiadiazole spectrum is presented in Fig. 3. The observed and

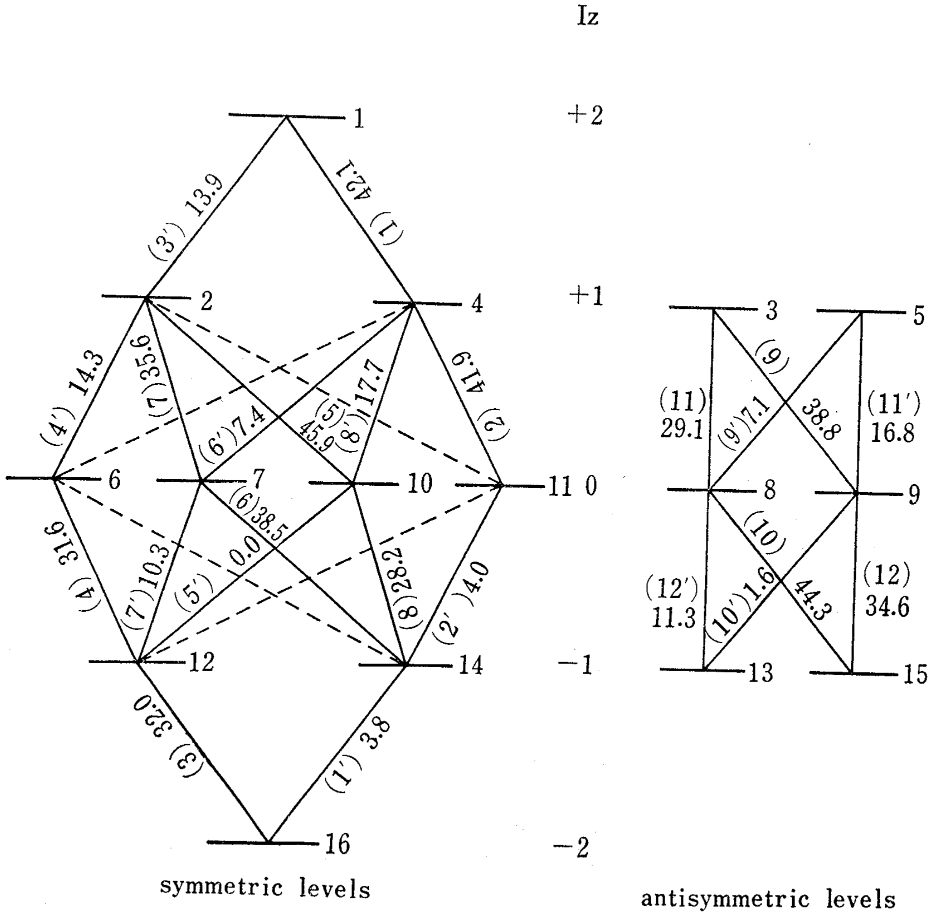

Fig. 3. The NMR Energy Level Diagram (Shematic) for Benzothiadiazole; Dashed Lines Represent Combination Transitions (not observed)

TABLE I

a) The converged magnetic parameters

| Compound | $\nu_0\delta_{AB}$ | $J_{AB}$ | $J_{BB'}$ | $J_{AB'}$ | $J_{AA'}$ |
|---|---|---|---|---|---|
| Benzoxadiazole | 25.21 | 9.05 | 6.49 | 0.86 | 1.27 |
| Benzothiadiazole | 26.33 | 8.96 | 6.65 | 1.16 | 0.90 |
| Benzoselenadiazole | 20.21 | 8.84 | 6.61 | 1.16 | 0.93 |
| Quinoxaline | 21.80 | 8.53 | 6.97 | 1.46 | 0.58 |

**All values are in cps.**

b) The observed and calculated spectra of quinoxaline

| Line | Transition | Obs. freq. | Calc. freq. | Calc. intensity |
|---|---|---|---|---|
| 5′ | $1_{-1}\rightarrow 5_0$ | 0.0 | 0.005 | 0.13 |
| 10′ | $2_{-1}\rightarrow 4_0$ | 1.3 | 1.25 | 0.17 |
| 1′ | $1_{-2}\rightarrow 3_{-1}$ | 3.6 | 3.56 | 1.17 |
| 2′ | $3_{-1}\rightarrow 6_0$ | 4.0 | 3.96 | 1.21 |
| 9′ | $3_0\rightarrow 4_1$ | 7.3 | 7.31 | 1.30 |
| 6′ | $2_0\rightarrow 3_1$ | 7.3 | 7.45 | 1.37 |
| 7′ | $1_{-1}\rightarrow 2_0$ | 9.6 | 9.66 | 1.59 |
| 12′ | $2_{-1}\rightarrow 3_0$ | 10.7 | 10.78 | 1.83 |
| 3′ | $1_1\rightarrow 1_2$ | 13.6 | 13.56 | 2.83 |
| 4′ | $1_0\rightarrow 1_1$ | 14.1 | 14.06 | 3.10 |
| 11′ | $4_0\rightarrow 4_1$ | 16.8 | 16.83 | 0.70 |
| 8′ | $5_0\rightarrow 3_1$ | 17.2 | 17.11 | 0.59 |
| 8 | $3_{-1}\rightarrow 5_0$ | 23.9 | 23.99 | 0.59 |
| 11 | $3_0\rightarrow 2_1$ | 24.3 | 24.26 | 0.70 |
| 4 | $1_{-1}\rightarrow 1_0$ | 27.0 | 27.03 | 3.10 |
| 3 | $1_{-2}\rightarrow 1_{-2}$ | 27.5 | 27.54 | 2.83 |
| 12 | $4_{-1}\rightarrow 4_0$ | 30.4 | 30.32 | 1.83 |
| 7 | $2_0\rightarrow 1_1$ | 31.5 | 31.44 | 1.59 |
| 6 | $3_{-1}\rightarrow 2_0$ | 33.8 | 33.65 | 1.37 |
| 9 | $4_0\rightarrow 2_1$ | 33.8 | 33.79 | 1.30 |
| 2 | $6_0\rightarrow 3_1$ | 37.1 | 37.14 | 1.21 |
| 1 | $3_1\rightarrow 1_2$ | 37.5 | 37.54 | 1.17 |
| 10 | $4_{-1}\rightarrow 3_0$ | 39.8 | 39.84 | 0.17 |
| 5 | $5_1\rightarrow 1_0$ | 41.1 | 41.09 | 0.13 |

**Frequencies are in cps and taken to be zero at the highest-field line.**

c) The observed and calculated spectra of benzoxadiazole

| Line | Transition | Obs. freq. | Calc. freq. | Calc. intensity |
|---|---|---|---|---|
| 5′ | $1_{-1}\rightarrow 5_0$ | 0.0 | 0.05 | 0.16 |
| 10′ | $2_{-1}\rightarrow 4_0$ | 1.8 | 1.80 | 0.25 |
| 1′ | $1_{-2}\rightarrow 3_{-1}$ | 4.3 | 4.25 | 1.41 |
| 2′ | $3_{-1}\rightarrow 6_0$ | 4.3 | 4.43 | 1.42 |
| 9′ | $3_0\rightarrow 4_1$ | 7.4 | 7.37 | 1.35 |
| 6′ | $2_0\rightarrow 3_1$ | 7.7 | 7.67 | 1.47 |
| 7′ | $1_{-1}\rightarrow 2_0$ | 10.5 | 10.50 | 1.74 |
| 12′ | $2_{-1}\rightarrow 3_0$ | 11.4 | 11.32 | 1.75 |
| 3′ | $1_1\rightarrow 1_2$ | 13.9 | 13.93 | 2.59 |
| 4′ | $1_0\rightarrow 1_1$ | 14.2 | 14.24 | 2.69 |
| 11′ | $4_0\rightarrow 4_1$ | 16.9 | 16.90 | 0.65 |
| 8′ | $5_0\rightarrow 3_1$ | 18.3 | 18.23 | 0.51 |
| 8 | $3_{-1}\rightarrow 5_0$ | 32.5 | 32.58 | 0.51 |
| 11 | $3_0\rightarrow 2_1$ | 33.9 | 33.91 | 0.65 |
| 4 | $1_{-1}\rightarrow 1_0$ | 36.6 | 36.56 | 2.69 |
| 3 | $1_{-2}\rightarrow 1_{-1}$ | 36.9 | 36.88 | 2.59 |
| 12 | $4_{-1}\rightarrow 4_0$ | 39.5 | 39.48 | 1.75 |
| 7 | $2_0\rightarrow 1_1$ | 40.3 | 40.30 | 1.74 |
| 6 | $3_{-1}\rightarrow 2_0$ | 43.1 | 43.13 | 1.47 |
| 9 | $4_0\rightarrow 2_1$ | 43.4 | 43.43 | 1.35 |
| 2 | $6_0\rightarrow 3_1$ | 46.5 | 46.38 | 1.42 |
| 1 | $3_1\rightarrow 1_2$ | 46.5 | 46.56 | 1.41 |
| 10 | $4_{-1}\rightarrow 3_0$ | 49.0 | 49.00 | 0.25 |
| 5 | $5_0\rightarrow 1_1$ | 50.8 | 50.86 | 0.16 |

**Frequencies are in cps and taken to be zero at the highest-field line.**

d) The observed and calculated spectra of benzothiadiazole

| Line | Transition | Obs. freq. | Calc. freq. | Calc. intensity |
|---|---|---|---|---|
| 5′ | $1_{-1}\rightarrow 5_0$ | 0.0 | 0.02 | 0.16 |
| 10′ | $2_{-1}\rightarrow 4_0$ | 1.6 | 1.60 | 0.23 |
| 1′ | $1_{-2}\rightarrow 3_{-1}$ | 3.8 | 3.78 | 1.28 |
| 2′ | $3_{-1}\rightarrow 6_0$ | 4.0 | 4.03 | 1.30 |
| 9′ | $3_0\rightarrow 4_1$ | 7.1 | 7.10 | 1.27 |
| 6′ | $2_0\rightarrow 3_1$ | 7.4 | 7.38 | 1.38 |
| 7′ | $1_{-1}\rightarrow 2_0$ | 10.3 | 10.31 | 1.67 |
| 12′ | $2_{-1}\rightarrow 3_0$ | 11.3 | 11.28 | 1.77 |
| 3′ | $1_1\rightarrow 1_2$ | 13.9 | 13.90 | 2.72 |
| 4′ | $1_0\rightarrow 1_1$ | 14.3 | 14.31 | 2.88 |
| 11′ | $4_0\rightarrow 4_1$ | 16.8 | 16.78 | 0.73 |
| 8′ | $5_0\rightarrow 3_1$ | 17.7 | 17.71 | 0.60 |
| 8 | $3_{-1}\rightarrow 5_0$ | 28.2 | 28.19 | 0.60 |
| 11 | $3_0\rightarrow 2_1$ | 29.1 | 29.11 | 0.73 |
| 4 | $1_{-1}\rightarrow 1_0$ | 31.6 | 31.59 | 2.88 |
| 3 | $1_{-2}\rightarrow 1_{-1}$ | 32.0 | 31.99 | 2.72 |
| 12 | $4_{-1}\rightarrow 4_0$ | 34.6 | 34.62 | 1.77 |
| 7 | $2_0\rightarrow 1_1$ | 35.6 | 35.59 | 1.67 |
| 6 | $3_{-1}\rightarrow 2_0$ | 38.5 | 38.52 | 1.38 |
| 9 | $4_0\rightarrow 2_1$ | 38.8 | 38.80 | 1.27 |
| 2 | $6_0\rightarrow 3_1$ | 41.9 | 41.87 | 1.30 |
| 1 | $3_1\rightarrow 1_2$ | 42.1 | 42.11 | 1.28 |
| 10 | $4_{-1}\rightarrow 3_0$ | 44.3 | 44.30 | 0.23 |
| 5 | $5_0\rightarrow 1_1$ | 45.9 | 45.92 | 0.16 |

**Frequencies are in cps and taken to be zero at the highest-field line.**

e) The observed and calculated spectra of benzoselenadiazole

| Line | Transition | Obs. freq. | Calc. freq. | Calc. intensity |
|---|---|---|---|---|
| 5′ | $1_{-1}\rightarrow 5_0$ | 0.0 | −0.13 | 0.14 |
| 10′ | $2_{-1}\rightarrow 4_0$ | 1.5 | 1.48 | 0.20 |
| 1′ | $1_{-2}\rightarrow 3_{-1}$ | 3.6 | 3.48 | 1.11 |
| 2′ | $3_{-1}\rightarrow 6_0$ | 3.6 | 3.74 | 1.13 |
| 9′ | $3_0\rightarrow 4_1$ | 6.7 | 6.77 | 1.15 |
| 6′ | $2_0\rightarrow 3_1$ | 7.1 | 7.18 | 1.29 |
| 7′ | $1_{-1}\rightarrow 2_0$ | 9.7 | 9.79 | 1.56 |
| 12′ | $2_{-1}\rightarrow 3_0$ | 11.0 | 11.03 | 1.80 |
| 3′ | $1_1\rightarrow 1_2$ | 13.5 | 13.48 | 2.89 |
| 4′ | $1_0\rightarrow 1_1$ | 14.0 | 13.97 | 3.18 |
| 11′ | $4_0\rightarrow 4_1$ | 16.4 | 16.32 | 0.85 |
| 8′ | $5_0\rightarrow 3_1$ | 17.2 | 17.10 | 0.69 |
| 8 | $3_{-1}\rightarrow 5_0$ | 22.3 | 22.42 | 0.69 |
| 11 | $3_0\rightarrow 2_1$ | 23.2 | 23.20 | 0.85 |
| 4 | $1_{-1}\rightarrow 1_0$ | 25.6 | 25.55 | 3.18 |
| 3 | $1_{-2}\rightarrow 1_{-1}$ | 26.0 | 26.03 | 2.89 |
| 12 | $4_{-1}\rightarrow 4_0$ | 28.6 | 28.49 | 1.80 |
| 7 | $2_0\rightarrow 1_1$ | 29.8 | 29.73 | 1.56 |
| 6 | $3_{-1}\rightarrow 2_0$ | 32.4 | 32.34 | 1.29 |
| 9 | $4_0\rightarrow 2_1$ | 32.8 | 32.75 | 1.15 |
| 2 | $6_0\rightarrow 3_1$ | 35.9 | 35.78 | 1.13 |
| 1 | $3_1\rightarrow 1_2$ | 35.9 | 36.04 | 1.11 |
| 10 | $4_{-1}\rightarrow 3_0$ | 38.0 | 38.04 | 0.20 |
| 5 | $5_0\rightarrow 1_1$ | 39.5 | 39.65 | 0.14 |

**Frequencis are in cps and taken to be zero at the highest-field line.**

calculated spectra are compared in Table I with the converged magnetic parameters. The observed relative line intensities were not expressed in figures because the overlapping of some lines prevents accurate measurements of the peak heights. The coupling constants are taken to be of the same signs since the calculated spectra best fit the observed line intensities.

From Table I, it is shown that the chemical shift $\nu_0\delta_{AB}$ tends to decrease as oxygen is replaced by sulfur, selenium, and carbon double bond, although discrepancy is seen in the sulfur displacement. At first sight, this reduction may be ascribed to the smaller electronegativity of the substituents causing the more delocalized $\pi$-electron distribution. In addition to this, the spectra showed a concurrent lowfield shift of the average chemical shift $(\nu_A+\nu_B)/2$, which may reasonably be correlated with an increased ring current effect. As a tentative explanation for the little difference of the $\nu_0\delta_{AB}$ between benzoxadiazole and benzothiadiazole, there is a d-orbital model picture11) for the conjugation of the sulfur atom. According to this model, a Hückel molecular orbital calculation using the empirically determined parameters for these compounds12) showed that the difference of the $\pi$-electron density between the A and B carbons is of the almost same magnitude between benzoxadiazole and benzothiadiazole. The observed low-field shifts of $(\nu_A+\nu_B)/2$ are also consistent with the fact that with its d-orbitals, sulfur shows greater ability to participate in conjugation than oxygen.

It is also interesting to compare the magnitudes of the coupling constants for the compounds employed here. As is well known, the analysis of AA'BB' spin system does not distinguish between $J_{AA'}$ and $J_{BB'}$ nor between $J_{AB}$ and $J_{AB'}$. To assign these coupling constants to particular pairs of protons in the molecule, the observed coupling constants were compared with the values13,14) obtained from independent measurements of the similar *ortho*-disubstituted benzenes. The final result of Table I is such that the ordinary magnitudes of $J_{\text{ortho}}$, $J_{\text{meta}}$ and $J_{\text{para}}$ in aromatic hydrocarbons are kept except somewhat anomalous relation between $J_{\text{meta}}$ and $J_{\text{para}}$. The magnitude of the two $J_{\text{ortho}}$ is larger in $J_{AB}$ $(=J_{A'B'})$ than in $J_{BB'}$ and this tendency is remarkable in the coupling constants of the all compounds except quinoxaline. This may be attributed to a diene structure in these compounds of which contribution is known from informations on the bond orders and bond lengths so as to be more predominant in the related compounds than quinoxaline. However, the magnitudes of the $J_{\text{ortho}}$ of these compounds do not show any quantitative correlation with the corresponding $\pi$-bond order nor with the corresponding C–C bond length; rather it seems that the magnitudes increase as the internal bond angle in the ring is increased and the neighboring CH bonds become closer together and overlap more. For benzoselenadiazole $C_A=118°$ and $C_B=123°$, for benzothiadiazole $C_A=120°$ and $C_B=121°$ while for benzoxadiazole the corresponding angles are both 120°.15) The counteracting relationship between the magnitudes of $J_{\text{para}}$ and $J_{\text{meta}}$ as is extremely shown in the reverse of the order between $J_{\text{para}}$ and $J_{\text{meta}}$ from quinoxaline to benzoxadiazole suggests the application of the McConnell's theory16) that deduces a negative contribution of $\pi$-electrons to $J_{\text{meta}}$ in even alternant aromatic hydrocarbons.

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