

Proton Magnetic Resonance of Symmetrical Molecules

III. The Analysis of A_2B_2 Spectra by Perturbation Methods: the $(AB)_2$ Approximation

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A_2B_2 spectra are amenable to analysis by perturbation techniques not only in the large-shift limit, but also in certain other cases. If one of the A-B coupling constants is much larger than the other coupling constants in the system, and if these other coupling constants are all small in comparison with the relative chemical shift, the $(AB)_2$ approximation may be applied. In this approximation the molecule is treated as two almost independent AB systems and the smaller couplings are introduced as perturbations. Expressions for the $(AB)_2$ transition frequencies to second order and for the intensities to lowest order are derived. As illustrations of the method, the proton resonance spectra of thieno[3,2-b]thiophene and of some *p*-disubstituted benzenes are analysed, and the results are compared with those obtained by numerical diagonalization. The A_2B_2X spectrum of *p*-nitrobenzaldehyde is similarly treated as two superimposed $(AB)_2$ spectra.

1. INTRODUCTION

In the foregoing paper (II) we discussed the analysis of large-shift A_2B_2 spectra by perturbation methods (the so-called A_2X_2 and $(AX)_2$ approximations¹). In these approximations the molecule could to a first approximation be regarded as being composed either of two almost independent A_2 and X_2 systems or — even simpler — of two almost independent AX systems, and the couplings between the systems were then introduced as perturbations. It was found that the simple second order perturbation expressions for the transition frequencies provide very good approximations to the exact solution, even in systems where the conditions underlying the approximations are no longer strictly fulfilled.

The approach used in the $(AX)_2$ approximation can be further extended to cases where the relative chemical shift is of the same magnitude as one of the A-B coupling constants. When one of the A-B coupling constants in an A_2B_2 system is much larger than the other couplings, the spectrum will have the rough shape of an AB quartet with additional fine structure of the AB bands.

This indicates that an approximation can be based on the assumption that the molecule consists of two identical weakly interacting AB systems and that the smaller coupling constants may be introduced as perturbations. The results of the analysis of the spectrum of thieno[3,2-b]thiophene along these lines were briefly reported earlier in paper I.²

2. THEORY

In the general A_2B_2 case the Hamiltonian matrix can be factorized to a large extent according to the spin and symmetry of the basis functions. Then there remain five 2×2 submatrices and one 4×4 submatrix belonging to the spin zero symmetrical states.³⁻⁵

In the present paper, as in our earlier papers in this series, we adhere to the commonly used notations³⁻⁵ for the NMR parameters in A_2B_2 systems:

$$\begin{array}{ccc}
 A(1) \leftarrow J_A \rightarrow A(2) & & K = J_A + J_B \\
 \uparrow & & L = J_A - J'_B \\
 J & \nearrow J' & M = J_A - J_B \\
 \downarrow & \swarrow & N = J + J' \\
 B(4) \leftarrow J_B \rightarrow B(3) & &
 \end{array}$$

The Hamiltonian matrix, as obtained when the basis functions are chosen as products of eigenfunctions of the A_2 and B_2 systems, respectively, has been given by Pople *et al.*^{4,5} For further discussion let us assume that $\nu_A > \nu_B$; this imposes no restriction, since ν_A and ν_B may not be distinguished from the analysis of an experimental spectrum. In Table 1 the transformed states from the diagonalization of the 2×2 matrices are given. The angles Φ , ϑ_a , ψ_+ , ψ_- , are defined by

$$\tan 2\Phi = N/(\nu_A - \nu_B), \quad \tan 2\vartheta_a = L/M, \quad \tan 2\psi_{\pm} = L/(\nu_A - \nu_B \pm M)$$

where all angles are on the main branch. The modified general expressions for the energies of the transformed states as given in paper II may now be applied. We can express the energies of the s_1' and s_{-1}' states in the usual notation,³⁻⁵ however, without renouncing the feature¹ of asymptotic identity between state functions and basis functions, because the assumption $\nu_A - \nu_B > 0$ will always render the term $\frac{1}{2} N \tan \Phi$ (which occurs in the modified expressions) equal to the positive square root: $+[(\nu_A - \nu_B)^2 + N^2]^{\frac{1}{2}}$. The eigenvalues of the transformed states thus obtained are reproduced in Table 1.

From the diagonalized part of the matrix, six of the twelve allowed transitions in a half-spectrum can now be accounted for. If these transitions can be assigned to experimental lines in an analysis part of the parameter set can thus be immediately calculated.

(A B)₂ approximation

In an A_2B_2 system where one of the AB coupling constants, say J , and the relative chemical shift $\nu_A - \nu_B$ are much larger than the remaining coupling constants, the problem of the 4×4 matrix can be tackled by perturbation

Table 1. Eigenfunctions and energies for the A_2B_2 system, except for the spin zero symmetrical states. The quantity CN is defined by: $CN = ((\nu_A - \nu_B)^2 + N^2)^{\frac{1}{2}}$.

State	Function	Energy
s_2	s_2	$\nu_A + \nu_B + \frac{1}{2}N + \frac{1}{2}K$
$1s_1'$	$1s_1\cos\Phi - 2s_1\sin\Phi$	$\frac{1}{2}(\nu_A + \nu_B) - \frac{1}{2}CN + \frac{1}{2}K$
$2s_1'$	$1s_1\sin\Phi + 2s_1\cos\Phi$	$\frac{1}{2}(\nu_A + \nu_B) + \frac{1}{2}CN + \frac{1}{2}K$
$1s_{-1}'$	$1s_{-1}\cos\Phi + 2s_{-1}\sin\Phi$	$-\frac{1}{2}(\nu_A + \nu_B) + \frac{1}{2}CN + \frac{1}{2}K$
$2s_{-1}'$	$-1s_{-1}\sin\Phi + 2s_{-1}\cos\Phi$	$-\frac{1}{2}(\nu_A + \nu_B) - \frac{1}{2}CN + \frac{1}{2}K$
s_{-2}	s_{-2}	$-(\nu_A + \nu_B) + \frac{1}{2}N + \frac{1}{2}K$
$1a_1'$	$1a_1\cos\psi_+ + 2a_1\sin\psi_+$	$\nu_B - \frac{1}{2}M - \frac{1}{2}K - \frac{1}{2}L \tan \psi_+$
$2a_1'$	$-1a_1\sin\psi_+ + 2a_1\cos\psi_+$	$\nu_A + \frac{1}{2}M - \frac{1}{2}K + \frac{1}{2}L \tan \psi_+$
$1a_0'$	$1a_0\cos\theta_a - 2a_0\sin\theta_a$	$\frac{1}{2}M - \frac{1}{2}K + \frac{1}{2}L \tan \theta_a$
$2a_0'$	$1a_0\sin\theta_a + 2a_0\cos\theta_a$	$-\frac{1}{2}M - \frac{1}{2}K - \frac{1}{2}L \tan \theta_a$
$1a_{-1}'$	$1a_{-1}\cos\psi_- - 2a_{-1}\sin\psi_-$	$-\nu_B - \frac{1}{2}M - \frac{1}{2}K + \frac{1}{2}L \tan \psi_-$
$2a_{-1}'$	$1a_{-1}\sin\psi_- + 2a_{-1}\cos\psi_-$	$-\nu_A + \frac{1}{2}M - \frac{1}{2}K - \frac{1}{2}L \tan \psi_-$

methods: the two AB systems are considered to be almost independent and the small coupling constants are introduced as perturbations. This approach will be denoted the $(AB)_2$ approximation.

In the $(AB)_2$ treatment the basis functions of the spin zero symmetrical states are chosen as symmetrical products of eigenfunctions for the AB systems, and the 4×4 matrix becomes approximately diagonal. The eigenfunctions of the A(1) B(4) system are ⁵

$$\begin{aligned} f_1(1,4) &= \alpha(1)\alpha(4) \\ f_2(1,4) &= \alpha(1)\beta(4) \cos\varphi + \beta(1)\alpha(4) \sin\varphi \\ f_3(1,4) &= -\alpha(1)\beta(4) \sin\varphi + \beta(1)\alpha(4) \cos\varphi \\ f_4(1,4) &= \beta(1)\beta(4) \end{aligned}$$

where the angle φ is defined from

$$\tan 2\varphi = J/(\nu_A - \nu_B)$$

The symmetrical spin zero products of the AB eigenfunctions are given in Table 2, where the spin products are in sequential order $\alpha(1)\beta(2)\alpha(3)\beta(4)$ etc. The corresponding matrix elements of the Hamiltonian are also listed in Table 2. From these we see that if $|J| \gg |J'|, |K|$, and if $(\nu_A - \nu_B)^2/|J| \gg |J'|, |K|$ then the 4×4 matrix is approximately diagonalized.

The "symmetry" of the constants J and J' is spoilt in this treatment, by the discriminate neglect of J' in the formation of the transformed s_0 states. Therefore, the advantage of using the symbols N and L is partially lost, and we shall in the following use a mixture of symbols: J, J', K and M for the s_0 states and K, L, M , and N for other states.

It is of course possible to take all the basis functions of the A_2B_2 systems as products of AB eigenfunctions in a manner analogous to the $(AX)_2$ treatment of paper II. However, no simplification of the expressions for the transition frequencies is thereby obtained so the exact treatment is retained where possible.

The diagonal elements of Table 2 give the energies of the spin zero symmetrical states to first order. Closed expressions can thus be derived for first

Table 2. Basis functions of the spin zero symmetrical states as products of AB eigenfunctions and corresponding matrix elements. The quantity CJ is defined by: $CJ = (\nu_A - \nu_B)^2 + J^2$.

Notation	Function	Product of AB eigenfunctions	Diagonal matrix elements	Off-diagonal matrix elements
$1s_0$	$\beta\beta\alpha\alpha \cos^2 \varphi + \alpha\alpha\beta\beta \sin^2 \varphi - (\alpha\beta\alpha\beta + \beta\alpha\beta\alpha) \sin \varphi \cos \varphi$	$f_3(1,4) \cdot f_3(2,3)$	$-CJ - \frac{1}{2}J + \frac{1}{4}(K - 2J') \cos^2 2\varphi$	$\langle 1s_0 H 2s_0 \rangle = \frac{1}{2}(\frac{1}{2}K - J') \sin^2 2\varphi$
$2s_0$	$\alpha\alpha\beta\beta \cos^2 \varphi + \beta\beta\alpha\alpha \sin^2 \varphi + (\beta\alpha\beta\alpha + \alpha\beta\alpha\beta) \sin \varphi \cos \varphi$	$f_2(1,4) \cdot f_2(2,3)$	$CJ - \frac{1}{2}J + \frac{1}{4}(K - 2J') \cos^2 2\varphi$	$\langle 1s_0 H 3s_0 \rangle = \frac{1}{2\sqrt{2}} \sin 4\varphi (\frac{1}{2}K - J')$ $\langle 1s_0 H 4s_0 \rangle = \frac{1}{\sqrt{2}} (J' - \frac{1}{2}K \sin 2\varphi)$
$3s_0$	$\frac{1}{\sqrt{2}} ((\alpha\beta\alpha\beta + \beta\alpha\beta\alpha) \cos 2\varphi + (\beta\beta\alpha\alpha - \alpha\alpha\beta\beta) \sin 2\varphi)$	$\frac{1}{\sqrt{2}} (f_2(1,4) \cdot f_3(2,3) + f_3(1,4) \cdot f_2(2,3))$	$-\frac{1}{2}J - \frac{1}{4}(K - 2J') \cos 4\varphi$	$\langle 2s_0 H 3s_0 \rangle = -\frac{1}{2\sqrt{2}} \sin 4\varphi (\frac{1}{2}K - J')$
$4s_0$	$\frac{1}{\sqrt{2}} (\alpha\beta\beta\alpha + \beta\alpha\alpha\beta)$	$\frac{1}{\sqrt{2}} (f_1(1,4) \cdot f_3(2,3) + f_4(1,4) \cdot f_1(2,3))$	$\frac{1}{2}(J - J') - \frac{1}{4}K$	$\langle 2s_0 H 4s_0 \rangle = \frac{1}{\sqrt{2}} (J' + \frac{1}{2}K \sin 2\varphi)$ $\langle 3s_0 H 4s_0 \rangle = \frac{1}{2}K \cos 2\varphi$

Table 2. Transition frequencies and intensities for the A transitions of an A_2B_2 system. The energies of the symmetrical spin zero states were obtained by the $(AB)_2$ approximation to first and second order, while the energies of the other states are exact. The quantities CJ and CN are defined by: $CJ = ((v_A - v_B)^2 + J^2)^{1/2}$, $CN = ((v_A - v_B)^2 + N^2)^{1/2}$.

Transition	Exact and to first order	Transition frequency relative to $\frac{1}{2}(v_A + v_B)$ Second order correction	Relative intensity
1. $1s_1' \rightarrow s_2$ 2. $1s_0' \rightarrow 1s_1'$	$\frac{1}{2}CN + \frac{1}{2}N$ $CJ + \frac{1}{2}J - \frac{1}{2}CN - \frac{1}{2}(K - 2J') \cos^2 2\varphi + \frac{1}{2}K$	$+\frac{1}{32} \cdot \frac{(K - 2J')^2 (4 - 3 \sin^2 2\varphi) \cdot \sin^2 2\varphi}{CJ} +$ $+\frac{1}{8} \cdot \frac{(K \sin 2\varphi - 2J')^2}{CJ + J}$	$\frac{1 - \sin 2\Phi}{(1 - \sin 2\varphi) \cos^2(\varphi - \Phi)}$
3. $s_{-2} \rightarrow 1s_{-1}'$ 4. $1s_{-1}' \rightarrow 2s_0$	$\frac{1}{2}CN - \frac{1}{2}N$ $CJ - \frac{1}{2}J - \frac{1}{2}CN + \frac{1}{2}(K - 2J') \cos^2 2\varphi - \frac{1}{2}K$	$+\frac{1}{32} \cdot \frac{(K - 2J')^2 (4 - 3 \sin^2 2\varphi) \cdot \sin^2 2\varphi}{CJ} +$ $+\frac{1}{8} \cdot \frac{(K \sin 2\varphi + 2J')^2}{CJ - J}$	$\frac{1 + \sin 2\Phi}{(1 + \sin 2\varphi) \cos^2(\varphi - \Phi)}$
5. $3s_0 \rightarrow 2s_1'$	$\frac{1}{2}CN + \frac{1}{2}J + \frac{1}{2}(K - 2J') \cos 4\varphi + \frac{1}{2}K$	$+\frac{1}{4} \cdot \frac{K^2 \cos^2 2\varphi}{J}$	$\frac{1}{2}(1 - \sin(4\varphi - 2\Phi))$
6. $2s_{-1}' \rightarrow 4s_0$	$\frac{1}{2}CN + \frac{1}{2}(J - J' - K)$	$+\frac{1}{8} \cdot \frac{(K \sin 2\varphi - 2J')^2}{CJ + J} - \frac{1}{8} \cdot \frac{(K \sin 2\varphi + 2J')^2}{CJ - J} +$ $+\frac{1}{4} \cdot \frac{K^2 \cos^2 2\varphi}{J}$	$\frac{1}{2}(1 - \sin 2\Phi)$
7. $4s_0 \rightarrow 2s_1'$	$\frac{1}{2}CN - \frac{1}{2}(J - J' - K)$	$-\frac{1}{8} \cdot \frac{(K \sin 2\varphi - 2J')^2}{CJ + J} + \frac{1}{8} \cdot \frac{(K \sin 2\varphi + 2J')^2}{CJ - J} -$ $-\frac{1}{4} \cdot \frac{K^2 \cos^2 2\varphi}{J}$	$\frac{1}{2}(1 + \sin 2\Phi)$
8. $2s_{-1}' \rightarrow 3s_0$	$\frac{1}{2}CN - \frac{1}{2}J - \frac{1}{2}(K - 2J') \cos 4\varphi - \frac{1}{2}K$	$-\frac{1}{4} \cdot \frac{K^2 \cos^2 2\varphi}{J}$	$\frac{1}{2}(1 + \sin(4\varphi - 2\Phi))$
9. $2s_0' \rightarrow 2a_1'$	$\frac{1}{2}(v_A - v_B) + M + \frac{1}{2}L(\tan \psi_+ + \tan \theta_a)$		$\sin^2(\theta_a - \psi_+)$
10. $2a_{-1}' \rightarrow 1a_0'$	$\frac{1}{2}(v_A - v_B) + \frac{1}{2}L(\tan \psi_- + \tan \theta_a)$		$\cos^2(\theta_a + \psi_-)$
11. $1a_0' \rightarrow 2a_1'$	$\frac{1}{2}(v_A - v_B) + \frac{1}{2}L(\tan \psi_+ - \tan \theta_a)$		$\cos^2(\theta_a - \psi_+)$
12. $2a_{-1}' \rightarrow 2a_0'$	$\frac{1}{2}(v_A - v_B) - M + \frac{1}{2}L(\tan \psi_- - \tan \theta_a)$		$\sin^2(\theta_a + \psi_-)$

order frequencies and zeroth order intensities of the transitions involving these states. These formulae are given in Table 3 (transitions number 2, 4, 5, 6, and 8) together with the *exact* expressions for those transitions (numbers 1, 3, 9, 10, 11, and 12) which do not involve the s_0 states. Simplified notations are used for the square roots.

If the requirements underlying the approximation are not strictly fulfilled, the perturbation treatment can easily be extended to second order. In Table 3 the second order corrections to the pertinent transition frequencies are also included. Here ordinary second order perturbation expressions were applied. To obtain a better estimate of relative intensities the perturbation treatment ought to be extended beyond zeroth order. The value of the higher order expressions is reduced, however, by the complexity of the expressions obtained and higher order intensity corrections will not be considered here.

3. ILLUSTRATIVE APPLICATIONS

The $(AB)_2$ perturbation treatment has been applied to the analysis of the spectra of thieno[3,2-b]thiophene, *p*-bromochlorobenzene, and *p*-chlorocyanobenzene. The A_2B_2X spectrum of *p*-nitrobenzaldehyde has been analysed in a similar manner as two superimposed A_2B_2 spectra. The spectra of the bromochloro- and chlorocyanobenzenes have been analysed earlier⁶⁻⁹ by other methods, and are included here only for the sake of illustration of the $(AB)_2$ method.

Experimental details. The *p*-disubstituted benzenes used in the investigation were commercial products. The thieno[3,2-b]thiophene was synthesized by Professor Salo Gronowitz in connection with an investigation of the ring-closure of some α -thienylthio substituted acids, the results of which have been published earlier.¹⁰

Argon was bubbled through the sample tubes to remove dissolved oxygen before sealing off. The spectra shown were recorded on a Varian A 60 spectrometer. The sweep was calibrated with the side-band technique, where the power line frequency of 50.00 ± 0.05 cps was used as modulation frequency. Additional recordings were made on a Varian Associates model V4300 B high resolution spectrometer operating at 40.000 Mcps.

Thieno[3,2-b]thiophene (thiophene)

The spectrum of an 11.7 % acetone solution of thieno[3,2-b]thiophene at 60 Mcps is shown in Fig. 1. As seen from the figure the spectrum has the rough appearance of an AB quartet in which the finite values of the long-range cross-ring couplings are reflected in the fine structure splittings of the quartet lines. Good values of $\nu_A - \nu_B$ and J can then immediately be obtained from the rough AB analysis, and the value of J (c. 5.2 cps) is in good agreement with the J_{23} coupling in thiophene.¹¹ In order to determine the long-range coupling constants, however, a detailed assignment of the spectral lines to theoretical transitions is required.

In an earlier study of this molecule,² when the values of the cross-ring couplings were totally unknown, a large number of spectra were calculated to cover all possible line assignments. The $(AB)_2$ formulas of Table 3 for transition frequencies (to second order) and intensities were programmed for the

IBM 1620 computer of this University. Inspection of the calculated spectra gave a few promising assignments that were more thoroughly investigated. In the final assignment the parameters were then adjusted until agreement in the transition frequencies within the experimental error was obtained. As the relative chemical shift is solvent dependent, the compound was studied in several solvents to get a variety of spectral shapes and thus a more certain assignment. The radio-frequency was also altered: spectra were recorded at both 40 Mcps and 60 Mcps.

As described in paper II, a program has now been set up to adjust the parameter set of an assignment to a least squares fit of experimental and theoretical transition frequencies. Here different approximations can be used for the transition frequencies including the exact treatment by numerical diagonalization. In order to compare the different approximative methods of analysing the thiophene spectrum, we have applied the least squares optimization process to the first and second order approximations in the $(AB)_2$, $(AX)_2$, and A_2X_2 treatments as well as to the exact treatment.

The results are collected in Table 4 where the parameters found have been rounded off to the nearest 0.05 cps, so that the precision claimed for the NMR parameters may be in keeping with the experimental accuracy. The root mean square deviations obtained with these values are also given.

It may be seen from Table 4 that the A_2X_2 and $(AX)_2$ approximations to first order can give only an estimate of the parameters and that the chemical shift in particular is badly reproduced. This was to be expected in the present

Table 4. Parameter sets (in cps) obtained for thieno[3,2-b]thiophene in an 11.7 % acetone solution using various approximations in addition to the exact treatment.

	Exact treatment	$(AB)_2$ approximation		$(AX)_2$ approximation		A_2X_2 approximation		
		First order	Second order	First order	Second order	First order	Restricted second order	General second order
$\nu_A - \nu_B$	10.80	10.80	10.80	12.05	10.75	12.05	10.75	10.75
J	5.25	5.35	5.25	5.40	5.30	5.30	5.30	5.25
J'	-0.20	-0.25	-0.20	-0.15	-0.10	-0.05	-0.10	-0.20
J_A	1.55	1.55	1.55	1.35	1.35	1.35	1.35	1.60
J_B	0.75	0.75	0.70	0.65	0.60	0.60	0.60	0.75
Root mean square deviation	0.04	0.10	0.04	0.08	0.07	0.08	0.07	0.04

case where the relative shift is only twice the largest AB coupling constant. The restricted second order corrections of the A_2X_2 approximation lead to an improvement of the shift parameter as does the $(AX)_2$ approximation to second order. The general second order A_2X_2 expressions, however, reproduce the parameters of the exact solution well within the uncertainty and also give a good fit to the spectrum as seen from the mean deviation.

The thiophene spectrum is particularly amenable to analysis by the $(AB)_2$ approximation, by which remarkably accurate results may be obtained.

Already the first order terms reproduce the exact solution within the uncertainty and the extension of the perturbation treatment to second order gives almost complete agreement with the result of the diagonalization procedure. Also the fit of calculated to measured spectral frequencies is very good, as seen from the mean deviation.

The compound was also studied in an 18.6 % solution in carbon disulphide; the spectrum of this sample at 60 Mcps is shown in Fig. 2. Here the relative chemical shift is smaller and the large shift approximations do not suffice for an accurate analysis, but the $(AB)_2$ approximation is entirely adequate as can be seen from Table 5, where the results of the least squares fits are given. Even the first order terms reproduce the parameters of the exact solution well within the uncertainty and give a good fit to the spectrum. The inclusion of the second order terms gives an even better fit and the exact solution is exactly reproduced. The $(AB)_2$ approximation is thus very successful in this case: the first order terms may be considered sufficient to get a reasonable accuracy.

Table 5. Parameter sets (in cps) obtained for thieno[3,2-b]thiophene in an 18.6 % carbon disulphide solution using the $(AB)_2$ approximation and the exact treatment.

	Exact treatment	$(AB)_2$ First order	$(AB)_2$ approximation Second order
$\nu_A - \nu_B$	7.75	7.70	7.75
J	5.25	5.30	5.25
J'	-0.20	-0.25	-0.20
J_A	1.55	1.50	1.55
J_B	0.70	0.70	0.70
Root mean square deviation	0.03	0.09	0.03

More than ten spectra were recorded for each of these two samples, and the accuracy in the line positions is better than 0.10 cps. To estimate the uncertainty in the parameters, the partial derivatives of the theoretical transition frequencies with respect to the parameters were calculated. Allowing an uncertainty in well-resolved lines of 0.10 cps and of 0.20 cps in overlapping lines, we can estimate the uncertainty in the parameters to be less than 0.10 cps.

The analysis of the spectra of the two solutes giving different relative chemical shifts show complete agreement in the coupling constants.

The α protons are expected to be less shielded than the β protons as in thiophene and the assignment of the couplings J and J' is obvious in the present case. The couplings J_A and J_B can however not be distinguished from the analysis. Thus, we give as a result $J = J_{23} = J_{56} = +5.25$ cps, $J' = J_{26} = J_{35} = -0.20$ cps, $J_A = +1.55$ cps and $J_B = +0.75$ cps.* The relative

* The absolute signs of coupling constants cannot be determined from the analysis; however, the *ortho* coupling in benzene has been found to be positive.¹²

chemical shift is solvent dependent. For the acetone solution we find $\nu_2 - \nu_3 = \nu_5 - \nu_6 = 0.180$ ppm, and for the carbon disulphide solution $\nu_2 - \nu_3 = \nu_5 - \nu_6 = 0.129$ ppm.

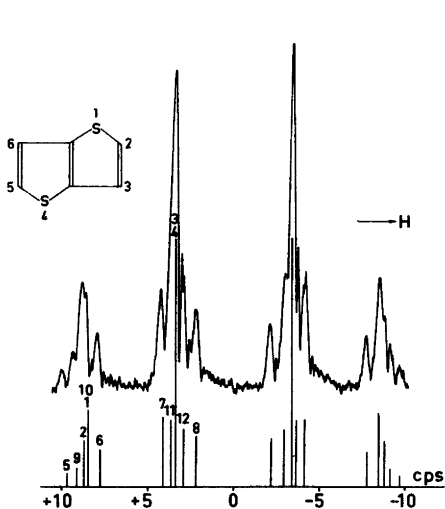


Fig. 1. NMR-spectrum at 60 Mcps of thieno[3,2-b]thiophene in an 11.7 % acetone solution. The experimental spectrum is fitted by the parameters (in cps): $\nu_A - \nu_B = 10.80$, $J = 5.25$, $J' = -0.20$, $J_A = 1.55$, and $J_B = 0.75$.

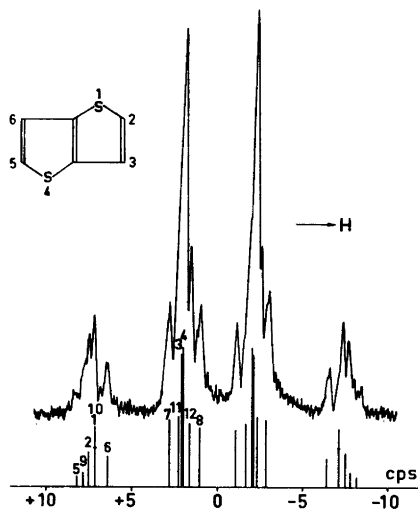


Fig. 2. The 60 Mcps spectrum of thieno[3,2-b]thiophene in an 18.6 % CS_2 solution. To fit the experimental spectrum a relative shift $\nu_A - \nu_B = 8.75$ cps and the same coupling constants as in Fig. 1 were used.

The theoretical spectra calculated with these parameters are given in Figs. 1 and 2. The parameters given here deviate slightly from those previously reported,² the small adjustment obtained here being due to the use of the least squares fit program now available. Of course the previously given set agrees well within the uncertainty.

p-Bromochlorobenzene and *p*-chlorocyanobenzene

The proton resonance spectra at 60 Mcps of *p*-bromochlorobenzene as a 38.0 % CS_2 solution and of *p*-chlorocyanobenzene as an 18.0 % CS_2 solution are shown in Figs. 3 and 4, respectively. From the values of the parameters previously given,⁶⁻⁹ a few spectra were calculated to confirm the assignments of experimental to theoretical lines. These assignments were then fed into the computer, and the results of the least squares fits obtained are summarized in Table 6, where rounded off values are given. Here only the $(AB)_2$ approximation is considered, since the relative shift is too small for the large shift approximations to be successfully applicable.

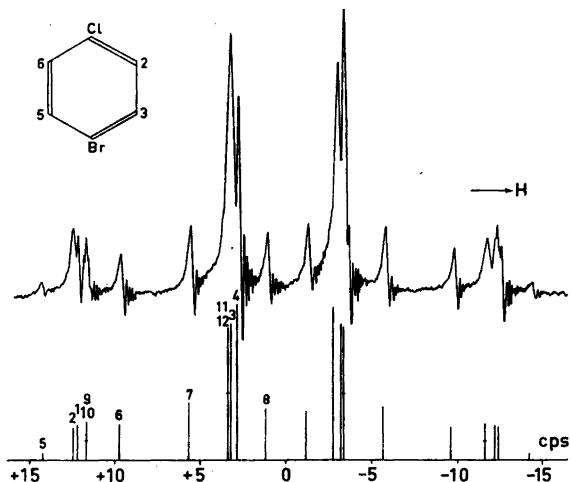


Fig. 3. Spectrum at 60 Mcps of *p*-bromochlorobenzene in a 38.0 % CS_2 solution. The theoretical spectrum is calculated with the parameters (in cps): $\nu_A - \nu_B = 12.50$, $J = 8.65$, $J' = 0.30$, and $J_A = J_B = 2.60$.

Several spectra were recorded in different solutions to ascertain the assignments. The uncertainty in the parameters obtained is as before estimated to be 0.10 cps. Theoretical spectra calculated with the parameters of the exact solution are included in Figs. 3 and 4.

In the *p*-bromochlorobenzene case, the first order terms provide good estimates of the parameters, and the extension of the approximation to second order gives a parameter set which reproduces that of the exact solution within

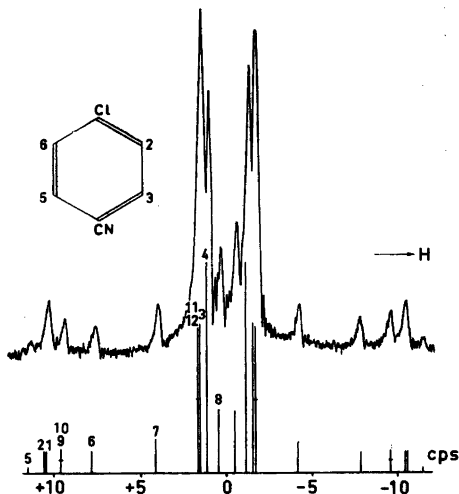


Fig. 4. The 60 Mcps spectrum of *p*-chlorocyanobenzene in an 18.0 % CS_2 solution. The theoretical spectrum is calculated with the parameters (in cps): $\nu_A - \nu_B = 8.05$, $J = 8.35$, $J' = 0.50$, and $J_A = J_B = 2.10$.

Table 6. Parameter sets (in cps) obtained for *p*-bromochlorobenzene and *p*-chlorocyanobenzene from the (AB)₂ approximation and the exact treatment.

	<i>p</i> -bromochlorobenzene			<i>p</i> -chlorocyanobenzene		
	Exact treatment	(AB) ₂ approximation First order	Second order	Exact treatment	(AB) ₂ approximation First order	Second order
$\nu_A - \nu_B$	12.50	12.45	12.45	8.05	8.25	8.00
J	8.65	8.85	8.70	8.35	8.30	8.45
J'	0.30	0.10	0.30	0.50	0.40	0.45
J_A	2.60	2.60	2.55	2.10	2.25	1.95
J_B	2.60	2.60	2.55	2.10	2.25	1.95
Root mean square deviation	0.04	0.24	0.05	0.05	0.16	0.10

the uncertainty. The fit of the calculated to the observed transition frequencies is then also satisfactory.

In *p*-chlorocyanobenzene the second order approximation does not give such a good fit, and the value of K does not agree with that of the exact solution; however, it is only slightly outside the uncertainty. This difficulty may be expected when CJ gets too close to J and at the same time K is not very small compared to J , because then the states $2s_0$ and $4s_0$ of Table 2 come close to degeneracy (*cf.* also the second order correction terms in Table 3). Therefore, in *p*-disubstituted benzenes the (AB)₂ approximation will give poor estimates of K and, to some extent, of CJ and J (*i.e.* of the shift and J_{ortho}) when the relative chemical shift is smaller than the *ortho* coupling constant.

In *p*-bromochlorobenzene the protons *ortho* to the bromo substituent may be expected to give the low field multiplet,^{9,13,14} which has also been directly confirmed by deuteration.⁸ The assignment of J and J' is obvious in this case also. Thus as a result we give: $\nu_A - \nu_B = \nu_3 - \nu_2 = \nu_5 - \nu_6 = 0.208$ ppm, $J = J_{23} = J_{56} = 8.65$ cps, $J' = J_{25} = J_{36} = 0.30$ cps and $J_A = J_B = J_{35} = J_{26} = 2.60$ cps. These values agree well with those previously given at comparable resolution by Grant, Hirst and Gutowsky,⁹ but deviate in J outside the uncertainty with those given by Dischler and Englert⁷ and Martin and Dailey.⁸

In *p*-chlorocyanobenzene the protons *ortho* to the cyano group may be expected to be shifted to lower field due to the electron attracting properties of this group,¹³⁻²² which has also been verified directly by deuteration.⁸ Thus we give as a result $\nu_A - \nu_B = \nu_2 - \nu_3 = \nu_6 - \nu_5 = 0.134$ ppm, $J = J_{23} = J_{56} = 8.35$ cps, $J' = J_{25} = J_{36} = 0.50$ cps and $J_A = J_B = J_{26} = J_{35} = 2.10$ cps. These values agree well with those previously given by Martin and Dailey.⁸

p-Nitrobenzaldehyde

We have also studied an A₂B₂X case, *p*-nitrobenzaldehyde, the A₂B₂ part of which has also been analysed by the (AB)₂ perturbation treatment. The spectrum of a 10.0 % acetone solution at 60 Mcps is shown in Fig. 5.

As has been discussed by Pople *et al.*^{23,24} the A_2B_2 part of the spectrum will consist of two overlapping A_2B_2 patterns, which as a first step in the analysis should be picked out. The separation of the centres of these patterns is then given by $\Delta = \frac{1}{2}(J_{AX} + J_{BX})$. The apparent relative chemical shifts for the two A_2B_2 multiplets are given by:

$$\delta\nu^+ = \nu_A - \nu_B + \frac{1}{2}(J_{AX} - J_{BX})$$

$$\delta\nu^- = \nu_A - \nu_B - \frac{1}{2}(J_{AX} - J_{BX})$$

As seen from the figure it is a straightforward procedure to pick out the two A_2B_2 patterns in the present case. The right-hand halves of the two patterns overlap completely while the left halves are separated by 0.50 cps. This splitting is clearly resolved in some of the lines. The two separate A_2B_2 spectra were then analysed in a manner analogous to the previous cases and the least squares fit with the $(AB)_2$ approximation to first and second order and the exact treatment was applied. The large shift approximations do not suffice here as expected due to the small relative shift.

Table 7. Parameter sets (in cps) obtained for one of the two A_2B_2 patterns in *p*-nitrobenzaldehyde from the $(AB)_2$ approximation and the exact treatment.

	Exact treatment	$(AB)_2$ approximation	
		First order	Second order
$\nu_A - \nu_B$	13.30	13.25	13.25
J	8.50	8.65	8.55
J'	0.50	0.35	0.50
J_A	1.85	1.95	1.85
J_B	2.35	2.35	2.30
Root mean square deviation	0.03	0.16	0.04

In Table 7 the results of the fits for the A_2B_2 multiplet with smallest shift are given; the values have been rounded off to the nearest 0.05 cps. As seen from the table the first order perturbation expressions give a good estimate of the parameters, only some of which deviate outside the uncertainty from the exact solution. By extension of the perturbation treatment to second order, better agreement with the exact solution is obtained: the two parameter sets differ by less than the uncertainty. The agreement with the experimental spectrum is also good as judged from the root mean square deviation.

The apparent relative shift is found to have the value of 13.30 cps, and is arbitrarily assigned to $\delta\nu^-$. The other A_2B_2 multiplet fitted in the same way gives $\delta\nu^+ = 13.80$ cps.

From the difference between the two apparent shifts, the difference between the aldehyde proton couplings to the *ortho* and *meta* positioned protons is found to have the magnitude of 0.50 cps. The separation of the midpoints of the two A_2B_2 patterns is half of this value, and the right halves of the patterns

overlap completely within the resolving power of the instrument. Thus we conclude that $J_{AX} = 0.50$ cps while J_{BX} is undetectably small. The relative sign of J_{AX} cannot be determined from this analysis; however, in related furan and thiophene compounds this coupling has been found to be positive.²⁵⁻²⁷

Both substituents are electron-attracting, but protons *ortho* to the nitro group may be expected to be more unshielded and give the down field multiplet.^{8,13-22} Thus the aldehyde proton couples only to its *meta* protons in this compound, a result which is consistent with findings in other aromatic compounds.^{20,21,28-35}

The *meta* couplings are both small, and the smaller one is attributed to the coupling across the nitro group which has the stronger electron-attracting properties.^{20,21,36-40}

Thus as a result we give

$$\nu_A - \nu_B = \nu_3 - \nu_2 = \nu_5 - \nu_6 = 0.226 \text{ ppm}$$

$$J = J_{23} = J_{56} = 8.50 \text{ cps}, J' = J_{25} = J_{36} = 0.50 \text{ cps},$$

$$J_A = J_{35} = 1.85 \text{ cps}, J_B = J_{26} = 2.35 \text{ cps and}$$

$$J_{AX} = J_{\text{CHO}-3} = J_{\text{CHO}-5} = 0.50 \text{ cps}.$$

The uncertainty in these values is estimated to be 0.15 cps in the same way as described above. The aldehyde proton shift is 10.25 ppm relative to tetramethylsilane as internal reference, while the aromatic proton shift $(\nu_A + \nu_B)/2$ is 8.32 ppm. The theoretical A_2B_2 spectrum calculated with these parameters is included in Fig. 5.

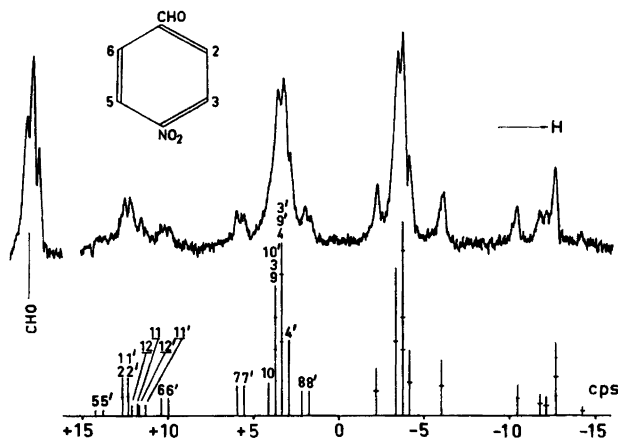


Fig. 5. Spectrum at 60 Mcps of *p*-nitrobenzaldehyde in a 10.0 % acetone solution. The A_2B_2 multiplet with the smallest apparent relative shift is fitted by the parameters (in cps): " $\nu_A - \nu_B$ " = 13.30, $J = 8.50$, $J' = 0.50$, $J_A = 1.85$, and $J_B = 2.35$. The theoretical lines for this multiplet are primed. The other A_2B_2 multiplet is displaced towards lower field by 0.25 cps and is fitted by the same coupling constants and an apparent relative shift of 13.80 cps.

4. CONCLUSIONS

In the analysis of A_2B_2 spectra, perturbation methods can be applied in favourable cases. The large shift approximations discussed in the previous paper (II) have been found to be applicable in several cases of intermediate coupling, with a ratio of coupling to shift ($J/(\nu_A - \nu_B)$) as large as 0.5 (*cf.* Table 4 of the present paper). Thus, the inclusion of second order terms in the perturbation treatments leads not only to good accuracy of the results for weakly coupled systems, but also to an extension of the range of possible applications.

For cases where the relative chemical shift is of the same magnitude as one of the A—B coupling constants, the $(AB)_2$ approximation discussed in the present paper may be used, provided that this coupling constant is much larger than the rest of the coupling constants. This type of spectrum is obtained, for example, with *p*-disubstituted benzenes where the perturbation treatment presented here should be applicable in most cases. Several such examples of analysis have been discussed in this paper. The perturbation treatment to second order was found to be almost as accurate as the analysis by exact diagonalization.

If the assumptions underlying the approximations are better fulfilled, the simple first order expressions will suffice for an accurate analysis, as was the case with the thieno[3,2-b]thiophene spectrum analysed in this paper.

If the relative shift gets small compared to the larger AB coupling constant, strong mixing appears between some of the spin zero symmetrical states as defined in Table 2, and the perturbation treatment here discussed will not work successfully. Even in cases where the relative shift is very large relative to the AB coupling constant the $(AB)_2$ perturbation treatment can of course be used, but then the much simpler $(AX)_2$ perturbation treatment introduced in the previous paper (II) is preferable.

By using the $(AB)_2$ approximation, the calculation time for a spectrum is considerably shortened in comparison with that required for the exact solution; the computation times on the computer are in the approximate proportions: [exact diagonalization]: [$(AB)_2$ to second order]: [$(AB)_2$ to first order] = 20: 2: 1.

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