Nuclear Magnetic Double Resonance in an ABX Spin System

The Signs of the Long-range Aldehyde Couplings in 2-Bromo-3-thiophenealdehyde

STURE FORSÉN,[a] BO GESTBLOM,[b] RAGNAR A. HOFFMAN,[b] and SÖREN RODMAR[b]

[a] Division of Physical Chemistry, Research Group for NMR, Royal Institute of Technology, Stockholm 70, Sweden
[b] Institute of Physics, University of Uppsala, Uppsala, Sweden

The sign of the side-chain coupling J_{CHO-5} relative to the ring coupling J_{45} in the ABX spectrum of 2-bromo-3-thiophenealdehyde has been determined by the use of nuclear magnetic double resonance. In one type of experiment, irradiation of a nearly degenerate doublet pair in the ring hydrogen band (AB) was employed to produce selective enlargement ("boosting") of the related unresolved doublet splitting in the aldehyde band (X). The interpretation of the results in terms of relative signs was entirely analogous to the procedure followed in selective decoupling experiments.

In addition, more general double irradiations of the AB band were performed and by comparison of the observed spectra with those calculated by numerical diagonalization of the complete double resonance Hamiltonian, it was also possible to derive the relative signs of the couplings J_{CHO-5} and J_{45}.

It was found that J_{CHO-5} and J_{45} carry the same sign. From the ABX analysis of the single resonance spectrum it was found that J_{CHO-4} is of opposite sign to J_{CHO-5}.

1. INTRODUCTION

It is generally agreed that the existence of nuclear spin couplings between nuclei, which are not directly bonded, depends upon a delocalization of the bonding electrons. The occurrence in certain molecules of couplings over four or more intervening bonds (long-range couplings) is therefore an indication of extensive electron delocalization in these systems. Long-range coupling has recently become the subject of intensive studies.[1] We have for some time been engaged in sign determinations of long-range couplings,[2-15] and we have found some interesting differences between the coupling patterns of the side-chain couplings of aromatic methyl and thiol compounds on the one hand

and the couplings of aromatic aldehyde and hydroxyl groups [16],[17] on the other. In previous work we have determined the signs of the side-chain couplings in 2- and 3-furanaldehydes [7] and of the side-chain coupling in 2-thiophene-aldehydes.[10] Only J_{CHO-4} in 3-furanaldehyde was found to be negative. In the present work we have determined the sign of the long-range aldehyde couplings in a 3-thiophenaldehyde.

The common procedure for sign determinations in first order (AMX) spectra is to apply the selective decoupling technique in which the splitting due to J_{AX} is eliminated in molecules with a definite spin state of the nucleus M thus giving the relative sign of J_{AM} and J_{MX}.[13],[18],[19] This method requires, however, that the signal from each nucleus has an observable structure caused by more than one pair of lines. In certain cases this condition will not be full-filled. In weakly coupled three spin systems with only two observable coupling constants for example, the determination of the relative signs necessitates the introduction of elaborate multiple resonance methods.[9],[10],[20]

In three-spin systems of the ABX type, however, the band assigned to each hydrogen consists in general of four lines and it may then be possible to perform a selective double irradiation experiment in order to establish the correct level arrangement. In an earlier paper we have demonstrated that the selective irradiation of one doublet pair in a pseudo-AX group (cf. Fig. 1) may be used to produce a collapse or an enlargement of the repeated splitting in the other doublet pair.[12] In the present paper we have used this technique to produce a selective enlargement of an unresolved splitting in the aldehyde band (X) of 2-bromo-3-thiophenealdehyde in order to determine the signs of the side-chain couplings relative to the ring coupling J_{45}. In addition we have performed more general double irradiations in which the ring hydrogen band was irradiated by a strong rf. field while the side-chain band was observed with a weak rf. field. This latter type of experiment could also be used for determining the signs of the side-chain couplings.

2. METHOD

If a strong irradiating rf. field of angular frequency ω_2 and amplitude $2H_2$ may be applied selectively, near two lines in a pseudo-AX group [12] (ω_{pq} and ω_{rs} in Fig. 1, say), while not perturbing any other lines having an energy level
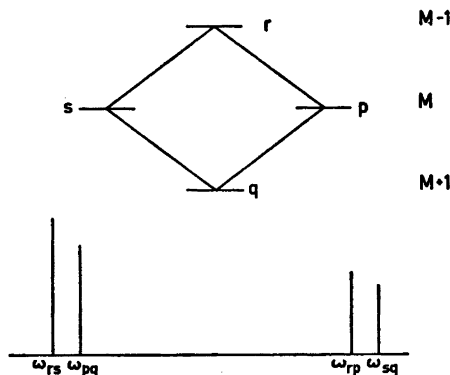

Fig. 1. Schematic energy level arrangement and transitions in a pseudo-AX system, i.e. a subsystem of four levels and four transitions in a general spectrum which form a closed polygon in the level diagram.

in common with the irradiated lines, the original doublet lines ω_{rp} and ω_{sq} will be transformed into a quartet. The frequencies of these quartet lines relative to ω_0, the center of the original doublet,

$$\omega_0 = \tfrac{1}{2}(\omega_{\mathrm{rp}} + \omega_{\mathrm{sq}}) \tag{1}$$

are given by:[12]

$$\omega'_{\mathrm{rp}} - \omega_0 = + A(pq) - A(rs) \tag{2}$$
$$\omega'_{\mathrm{rq}} - \omega_0 = - A(pq) - A(rs) \tag{3}$$
$$\omega'_{\mathrm{sq}} - \omega_0 = - A(pq) + A(rs) \tag{4}$$
$$\omega'_{\mathrm{sp}} - \omega_0 = + A(pq) + A(rs) \tag{5}$$

where $A(pq)$, $A(rs)$ are defined as

$$A(pq) = \pm \tfrac{1}{2}[(\omega_2 - \omega_{\mathrm{pq}})^2 + h_{\mathrm{pq}}^2]^{\frac{1}{2}} \tag{6}$$
$$A(rs) = \pm \tfrac{1}{2}[(\omega_2 - \omega_{\mathrm{rs}})^2 + h_{\mathrm{rs}}^2]^{\frac{1}{2}} \tag{7}$$

The $\pm$ signs indicate that the square roots are to carry the same signs as $(\omega_2 - \omega_{\mathrm{pq}})$ and $(\omega_2 - \omega_{\mathrm{rs}})$, respectively: h_{pq} and h_{rs} are abbreviations for $2\gamma H_2 \lambda_{\mathrm{pq}}$ and $2\gamma H_2 \lambda_{\mathrm{rs}}$, respectively, where λ_{pq} is the transition matrix element

$$\lambda_{\mathrm{pq}} = (\psi_{\mathrm{p}} | \Sigma_i I_i^x | \psi_{\mathrm{q}}) \tag{8}$$

The relative intensities of these lines are proportional [12] to the squares of the matrix elements of $\Sigma_i I_i^x$ between the mixed states ψ_{p}', ψ_{q}', ψ_{r}' and ψ_{s}'.

$$I_{\mathrm{rp}}' = 4 \times (\lambda_{\mathrm{rp}} \cos \varphi_{\mathrm{pq}} \cos \varphi_{\mathrm{rs}} + \lambda_{\mathrm{sq}} \sin \varphi_{\mathrm{pq}} \sin \varphi_{\mathrm{rs}})^2 \tag{9}$$
$$I_{\mathrm{rq}}' = 4 \times (\lambda_{\mathrm{rp}} \sin \varphi_{\mathrm{pq}} \cos \varphi_{\mathrm{rs}} - \lambda_{\mathrm{sq}} \cos \varphi_{\mathrm{pq}} \sin \varphi_{\mathrm{rs}})^2 \tag{10}$$
$$I_{\mathrm{sq}}' = 4 \times (\lambda_{\mathrm{rp}} \sin \varphi_{\mathrm{pq}} \sin \varphi_{\mathrm{rs}} + \lambda_{\mathrm{sq}} \cos \varphi_{\mathrm{pq}} \cos \varphi_{\mathrm{rs}})^2 \tag{11}$$
$$I_{\mathrm{sp}}' = 4 \times (\lambda_{\mathrm{rp}} \cos \varphi_{\mathrm{pq}} \sin \varphi_{\mathrm{rs}} - \lambda_{\mathrm{sq}} \sin \varphi_{\mathrm{pq}} \cos \varphi_{\mathrm{rs}})^2 \tag{12}$$

where the angles φ_{pq} and φ_{rs} are defined by

$$\tan 2\,\varphi_{\mathrm{pq}} = h_{\mathrm{pq}}/(\omega_2 - \omega_{\mathrm{pq}}) \tag{13}$$
$$\tan 2\,\varphi_{\mathrm{rs}} = h_{\mathrm{rs}}/(\omega_2 - \omega_{\mathrm{rs}}) \tag{14}$$

and where the angles φ are chosen on the main branch of the tangent function

$$-\pi/2 < 2\varphi < + \pi/2 \tag{15}$$

An examination of the expressions $(2) - (12)$ shows that it is always possible to bring two of the four lines to coalescence at ω_0 by adjusting the irradiation frequency and amplitude so as to satisfy the condition

$$\omega_2 = \tfrac{1}{2}(\omega_{\mathrm{pq}} + \omega_{\mathrm{rs}}) + \tfrac{1}{2}(h_{\mathrm{pq}}^2 - h_{\mathrm{rs}}^2)(\omega_{\mathrm{pq}} - \omega_{\mathrm{rs}})^{-1} \tag{16}$$

If the intensities of the two original doublet lines I_{rp} and I_{sq}, are not too unequal it will also be possible to accumulate most of the original doublet intensity in the coalesced lines. This result is similar to that obtained in a selective decoupling experiment in a first order spectrum.

If the intensities I_{pq} and I_{rs} of the two irradiated lines are significantly unequal the effect of a very strong irradiation in the neighbourhood of these lines will always result in a shift of all the four lines $(2) - (5)$ away from ω_0. For a given irradiation amplitude the separation of the two central lines will be maximized when ω_2 is chosen so as to give $\varphi_{\mathrm{pq}} = \varphi_{\mathrm{rs}} = \varphi$ and this maxi-

mum separation is then given by $(\omega_{rp} - \omega_{sq})/\cos 2\varphi$. Also in this case it is possible to retain most of the original intensity in the two central lines if I_{rp} and I_{sq} are not too unequal. This latter type of experiment represents in fact a selective enlargement ("boosting") of the original splitting and may also be used for the determination of the energy level arrangement. The selective enlargement (or "boosting") experiment may also be successfully performed in spectra where the repeated splitting is too small to be resolved, thus rendering impossible a selective decoupling experiment as is the case in the spectrum studied here. For a more extensive discussion of these methods; cf. Ref. 12.

In certain cases the rf. amplitude required to produce observable "boosting" effects may be too large to permit selective irradiation at ω_{pq} and ω_{rs}. In such cases it will be necessary to carry out a complete numerical diagonalization of the double resonance Hamiltonian [12],[21] in order to calculate the spectrum to be observed. Provided that significantly different spectra are expected for different sign alternatives these general double irradiation experiments may be as informative as the selective irradiation experiments. In the present study we have performed both selective enlargement ("boosting") and general double irradiation experiments.

3. EXPERIMENTAL

The spectra were obtained using a Varian Associates model V 4300 B spectrometer operating at a radiofrequency of 40.000 Mc/s. The spectra were recorded by use of phase sensitive detection by operating the Varian V 3521 integrator in the lower side-band mode. Additional single resonance spectra were obtained using a Varian A—60 spectrometer. The strong rf. field H_2 was obtained through frequency modulation of the rf. transmitter with a Philips audio oscillator model PP 6050. The audio frequencies were monitored with a Hewlett-Packard frequency counter model 524 D. Spectra were calibrated by the use of the side-band technique.

The amplitudes of the rf. field H_2 employed in the double resonance experiments were too low to be conveniently determined by the technique of Anderson [22],[23] and were instead determined by interpolation from a large number of double resonance transition curves calculated with different H_2 amplitudes to obtain the best fit with the observed X-part of the double resonance spectra (cf. also Ref. 12). The double resonance spectra were recorded by the field sweep method. The modulating frequency was altered in small steps to cover the entire AB multiplet while studying the CHO (X) pattern with the weak observing rf. field H_1.

The sample of 2-bromo-3-thiophenealdehyde used in this investigation was kindly synthesized by Fil.mag. R. Håkansson.

The theoretical double resonance spectra obtained by numerical diagonalization of the double resonance Hamiltonian were calculated on the Univac 1107 electronic computer of Norsk Regnesentral, Oslo, Norway, and Figs. 4 and 5 reproduce the direct output from the highspeed printer.

4. RESULTS AND DISCUSSION

The proton magnetic resonance spectrum at 40 Mc/s of 2-bromo-3-thio-phenealdehyde in a 30 % solution in cyclohexane is shown in Fig. 2. ABX
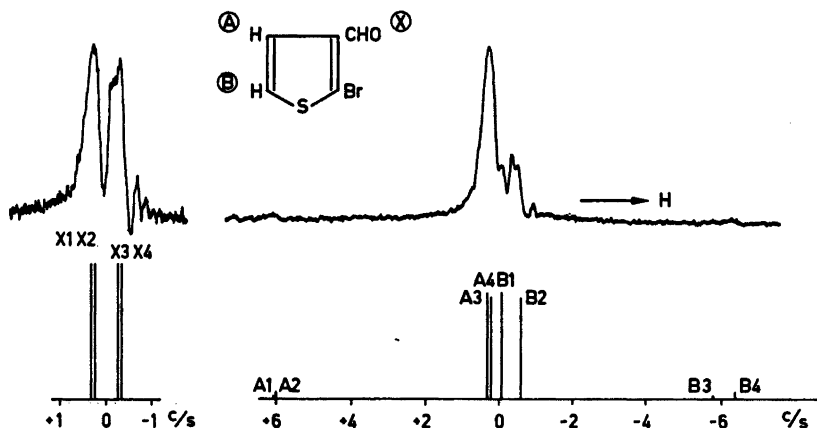

Fig. 2. The PMR spectrum at 40 Mc/s of 2-bromo-3-thiophenealdehyde. The schematic ABX-spectrum has been calculated with the parameters (in c/s) : $\nu_A - \nu_B = 2.70$; $J_{AB} = 5.80$; $J_{AX} = \mp 0.25$; $J_{BX} = \pm 0.90$. The lines are labelled (A,B,X) according to the origin of the transitions and numbered in sequential order.

analyses [24] of the spectra obtained at 40 Mc/s and at 60 Mc/s gave the following set of parameters valid at 40 Mc/s: $\nu_A - \nu_B = 2.70$ c/s, $J_{AB} = 5.80$ c/s, $J_{AX} = \mp 0.25$ c/s, and $J_{BX} = \pm 0.90$ c/s. The two distinct energy level diagrams consistent with these parameters are depicted in Fig. 3. The smallest repeated
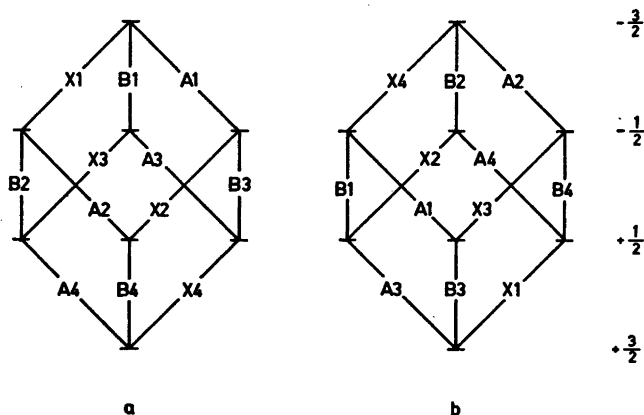

Fig. 3. The two distinct level diagrams consistent with the spectrum in Fig. 2. (a) corresponds to the case when J_{AB} and J_{BX} carry the same sign, (b) to the case when J_{AB} and J_{BX} carry opposite signs. The transitions are numbered as in Fig. 2. The combination lines are not included.

ABX DOUBLE RESONANCE
DAB= 2.70000 JAB= 5.79999 JAX= -.25000 JBX= .90000
AMPLITUDE: 4.00000   PLOT LINE FREQUENCY VS. OFFSET

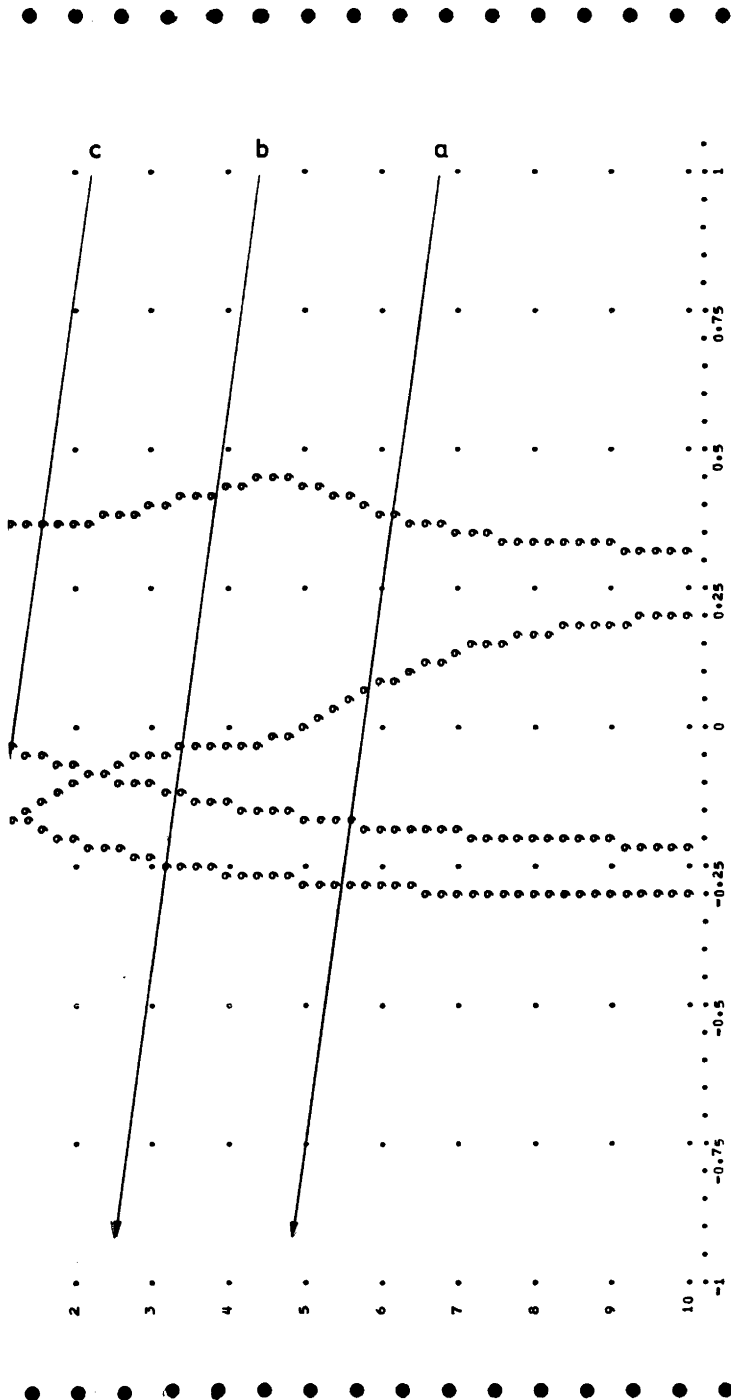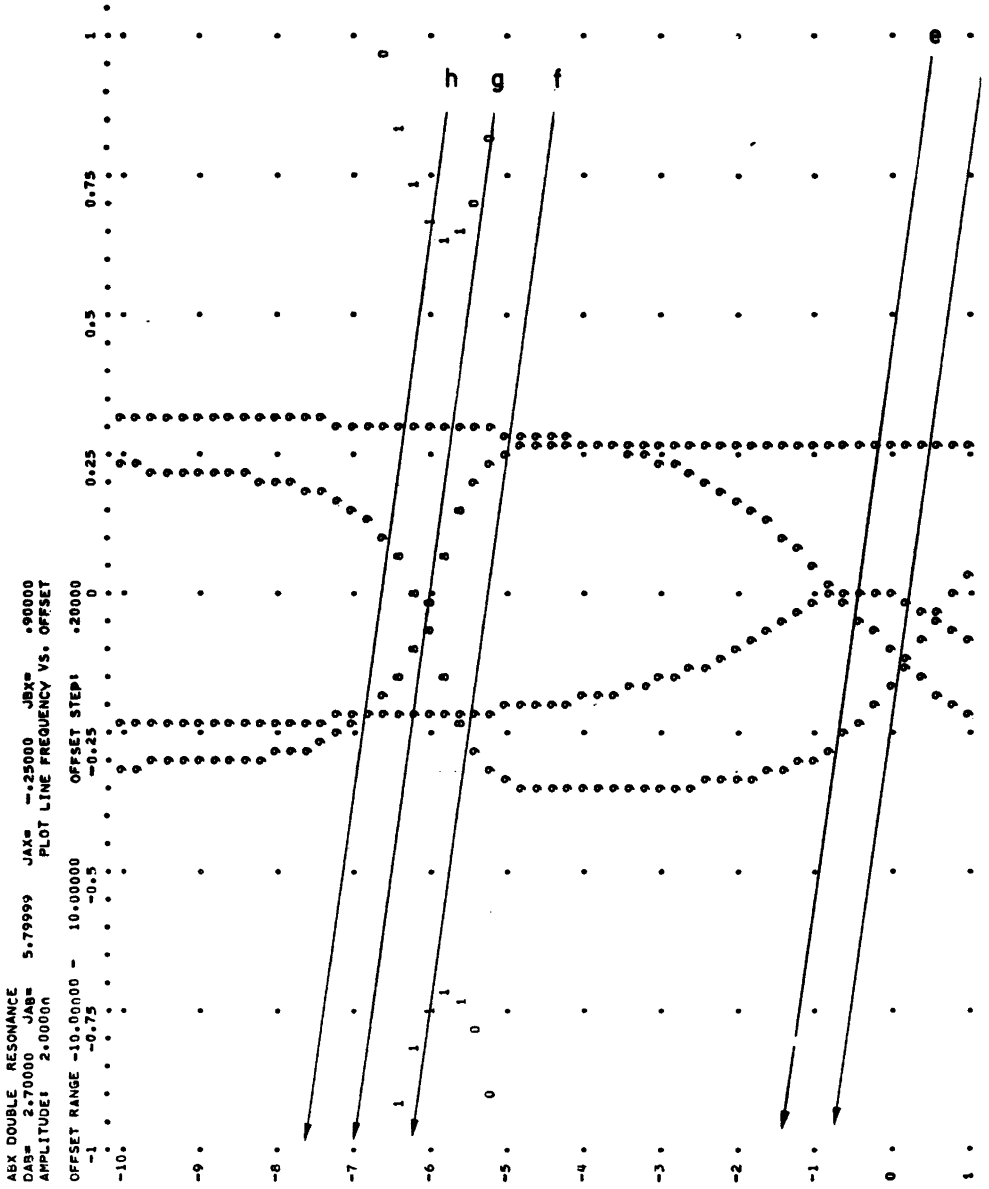OFFSET RANGE -10.00000 - 10.00000   OFFSET STEP: - .20000
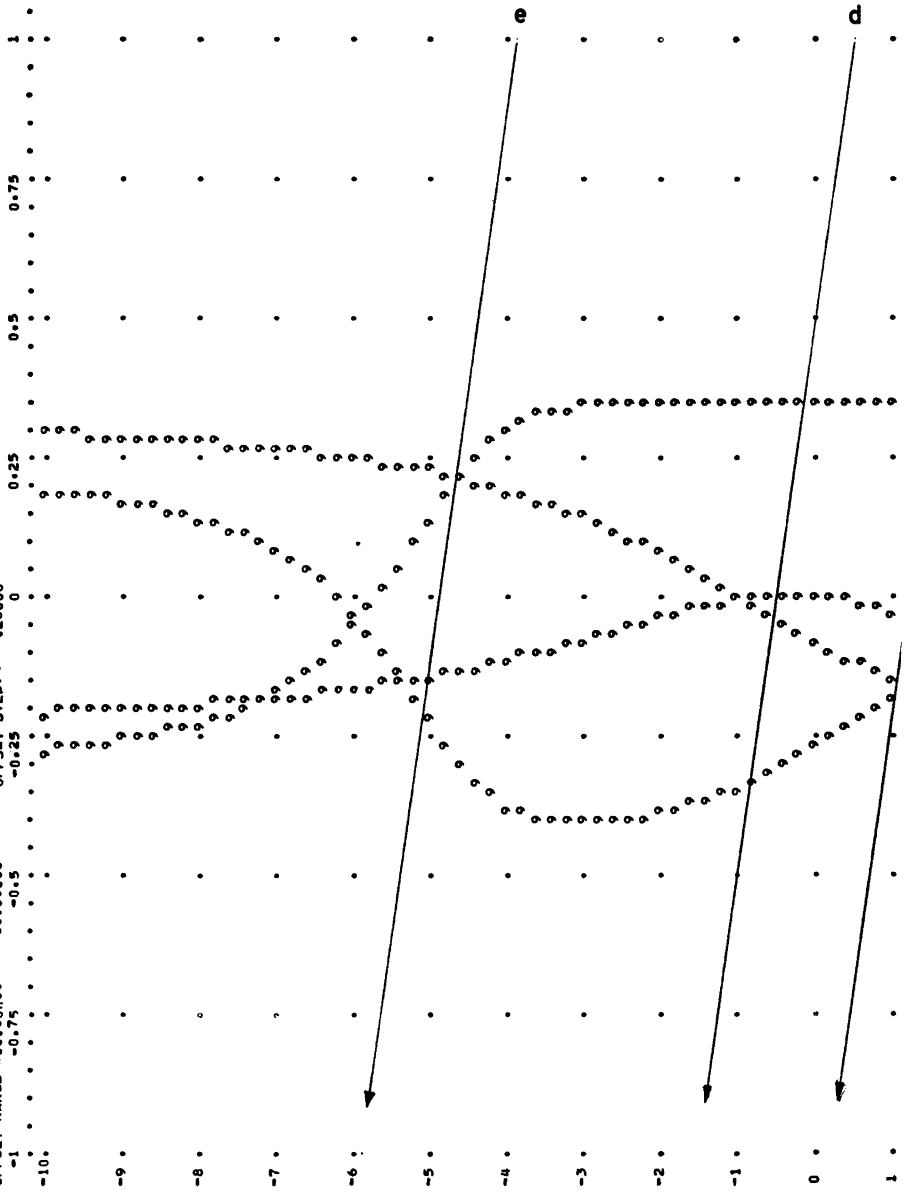
Fig. 4. Transition frequencies and intensities of the X-part in the spectrum of 2-bromo-3-hiophenealdehyde when the AB band is irradiated with a r.f. field with an amplitude $\gamma H_2/2\pi = 4.0$ c/s. The ordinate gives the offset $\nu_2 - (\nu_A + \nu_B)/2$ of the irradiating r.f. field H_2. The abscissa gives the frequency $\nu_1 - \nu_X$ of the transitions in the X- (CHO)-part observed with a weak r.f. field H_1. The relative line intensities have been employed in plotting the transition curves.

ABX DOUBLE RESONANCE
DAB= 2.70000   JAB= 5.79999   JAX= -.25000   JBX= .90000
AMPLITUDE: 2.0000n

OFFSET RANGE -10.00000 - 10.00000   OFFSET STEP: .20000
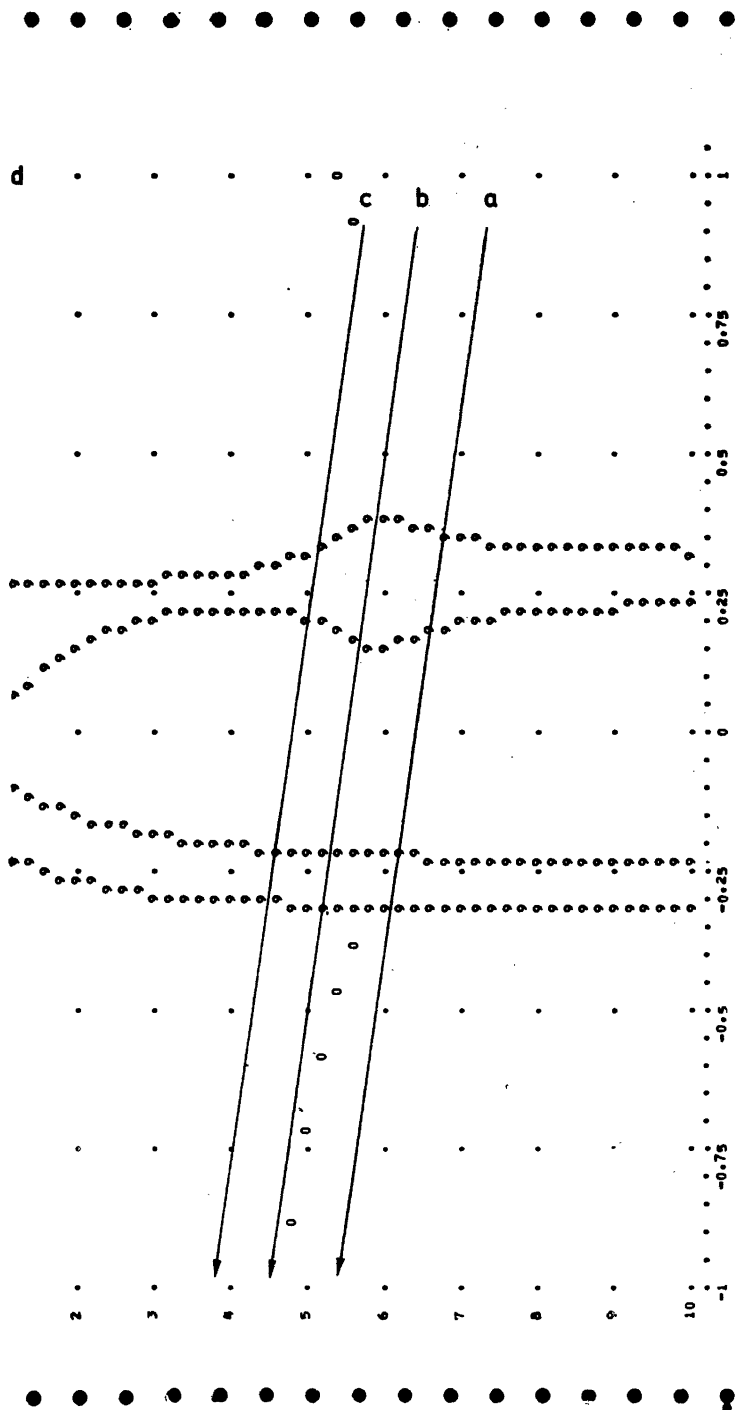PLOT LINE FREQUENCY VS. OFFSET

Fig. 5. Transition frequencies and intensities as in Fig. 4 but with an rf. amplitude $\gamma H_2/2\pi = 2.0$ c/s.

spacing, for example that occurring between the lines X1 and X2, is only 0.08 c/s in magnitude and thus precludes the possibility of performing a successful selective decoupling experiment. The intensities calcuted for the two overlapping lines A1 and A2 are 0.13 and 0.06, respectively. These intensities are sufficiently different to make a selective "boosting" experiment feasible. In the relatively strongly coupled ABX system studied here it should also be possible to obtain the relative signs of the spin coupling constants by producing characteristic asymmetries in the X-band by strong (non-selective) irradiation at certain frequencies in the AB-band.

4.1. ANALYSIS OF OBSERVED SPECTRA

To analyse the aldehyde (X) multiplets obtained in these experiments we have calculated the transition frequencies and intensities in the X-band by complete diagonalization of the double resonance Hamiltonian for the ABX case. The matrix elements in the general ABC case have been given by Rao and Baldeschwieler.[21] In the ABX case, when the irradiating H_2 field is applied in the AB-part, the Hamiltonian matrix may be factorized into two 4×4 submatrices where each submatrix belongs to a definite spin state of the X-nucleus. Since F_z is no longer a good quantum number the selection rule $\Delta F_z = \pm 1$ breaks down, and the only remaining selection rule is $\Delta I_z(X) = \pm 1$. The X-part of the spectrum will thus contain sixteen lines but many of these will have a negligible intensity. The occurrence of 4×4 matrices necessitates the use of an electronic computer for the numerical diagonalization of the matrices. With a high speed computer a large number of theoretical spectra are easily obtained. A graphical representation of the results is almost indispensable, in order to make the large amount of output data manageable. It is expedient to employ a high speed printer to plot the output of the computer and to utilize the actual relative intensities in plotting the theoretical transition curves.

Two such diagrams calculated with different irradiating amplitudes are shown in Figs. 4 and 5. In these figures the ordinate gives the offset $y = \nu_2 - (\nu_A + \nu_B)/2$ of the irradiating rf. field H_2 with the frequency ν_2. The abscissa gives the frequencies $x = \nu_1 - \nu_X$ of the transitions in the X — (CHO-) part observed with a weak rf. field H_1 with the frequency ν_1 relative to the center of the X-band (ν_X). In the transition curves a figure 9 denotes that the relative intensity lies between 0.9 and 1.0 and a figure 8 that the intensity lies between 0.8 and 0.9 etc. (The intensity 1.0 is the intensity of the lines X1 and X4 (Fig. 2) in the single resonance spectrum). Lines with an intensity lower than 0.01 have not been included since these would be far below the noise level of the spectrometer. Only transitions in the neighbourhood of ν_X (± 1 c/s) are plotted. The graphs in Figs. 4 and 5 have been calculated assuming that J_{AB} and J_{BX} have the same sign. A sign reversal of J_{AB} will result in a reflection of the diagrams in the ordinate, as may be deduced from the form of the matrix elements. A frequency swept spectrum, in which only ν_1 is changed, is obtained by intersecting the transition curves with a straight line parallel to the abscissa.

In a field sweep spectrum $(\nu_A + \nu_B)/2$ and ν_X change simultaneously. Such a spectrum in which the field goes from low to high field is obtained by intersecting the transition curves with a straight line as indicated by the arrows in the diagrams. It should be noted that the frequency scales of the ordinate and the abscissa are not equal. In the present work the field sweep technique was employed. By "offset" we will in the following mean the difference $y - x$.

At low irradiation amplitudes it is possible to irradiate the doublets A1, A2 or B3, B4 selectively without perturbing the central lines in the AB band. In this case the pseudo-AX theory presented in section 2 may be used to calculate theoretical spectra for the X-multiplet. An example of such a diagram calculated for the same irradiating amplitude as that used in calculating Fig. 5 is shown in Fig. 6. The form of presentation in Fig. 6 is the same as in Fig. 5
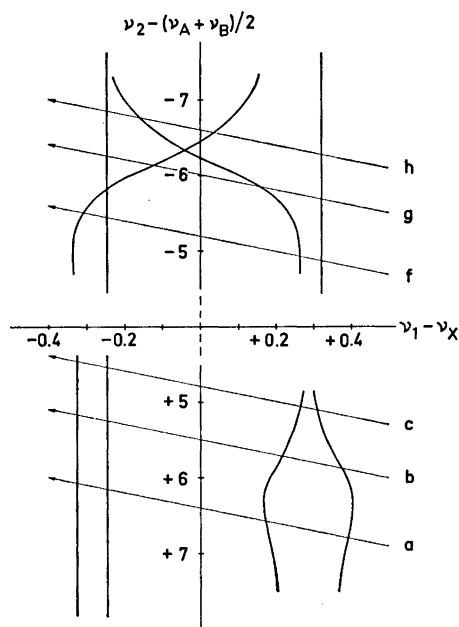
Fig. 6. Transition frequencies as in Figs. 4 and 5 calculated by use of the pseudo-AX theory. The rf. amplitude is the same as in Fig. 5, $\gamma H_2/2\pi = 2.0$ c/s. Only offsets corresponding to selective irradiation of the doublets A_1, A_2 or B_3, B_4 are considered. The calculated intensities are not included.

with the exception that the calculated intensities are not shown. It is seen that the two sets of calculated transition curves in Figs. 5 and 6 are similar in their general appearance. A closer inspection reveals, however, that some quantitative differences exist. For example the collapse of lines X2 and X4 is predicted to occur at an offset of -6.3 c/s from the pseudo-AX theory as compared to -6.1 c/s from numerical diagonalization of the full double resonance Hamiltonian. Similarly the offset required for optimum "boosting"

is numerically larger in the pseudo-AX theory. These discrepancies may be attributed to the fact that with the irradiation amplitude employed, more than two lines are perturbed by the double irradiation in violation of the basic assumption in the pseudo-AX theory.

4.2. EXPERIMENTAL DOUBLE RESONANCE SPECTRA

Two series of experiments were performed — one with an irradiation amplitude $\gamma H_2/2\pi$ of 4 ± 1 c/s and one with an amplitude of 2.0 ± 0.5 c/s. Both series cover a wide range of offsets. Some representative spectra are displayed in Figs. 7 and 8. The upper row (I) of theoretical spectra in Fig. 7
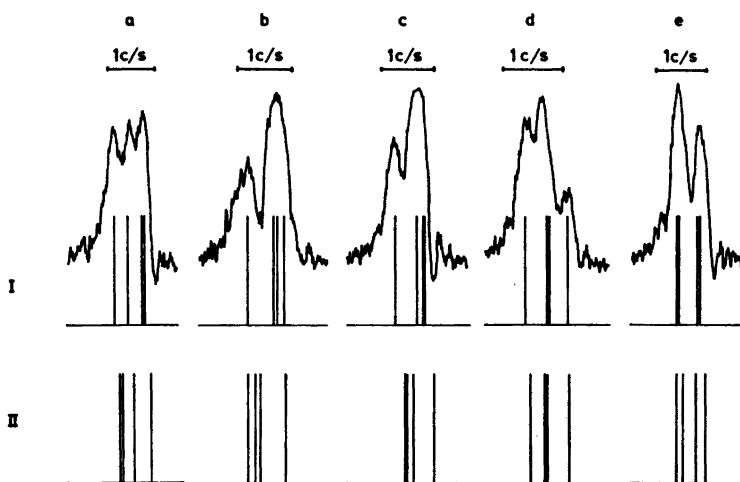

Fig. 7. Observed and predicted double resonance spectra of the X- (CHO-) part at various offsets with an rf. amplitude $\gamma H_2/2\pi = 4$ c/s. The offsets of the irradiating H_2-field $(y - x)$ are in c/s: a) $+ 5.7$, b) $+ 3.4$, c) $+ 1.2$, d) -1.5, e) -4.9. The theoretical spectra in set (I) were calculated assuming $J_{45} \times J_{CHO-5} > 0$ by use of Fig. 4. The field sweep lines corresponding to Figs. a)-e) are indicated in Fig. 4. Set (II) was obtained from a recast form of Fig. 4 to correspond to the assumption $J_{45} \times J_{CHO-5} < 0$ (*cf.* text).

was obtained under the assumption that $J_{AB} \times J_{BX} > 0$; the theoretical spectra in Figs. 7 a—e were obtained from the intersection of the corresponding arrow lines in Fig. 4. The lower row (II) of theoretical spectra was calculated under the assumption that $J_{AB} \times J_{BX} < 0$ and were obtained from Fig. 4 by reflection of the calculated transition curves in the ordinate. It may be noted that the experimental spectra displayed in Figs. 7 b and c are in good agreement with those calculated for equal signs of J_{AB} and J_{BX} but in obvious disagreement with those calculated for unlike signs of these two couplings. The spectra displayed in Figs. 7 a, 7 d, and 7 e are not sufficiently unsymmetrical to permit an unambiguous sign determination. A close inspection of the observed spectra indicates, however, that a better agreement between calculat-
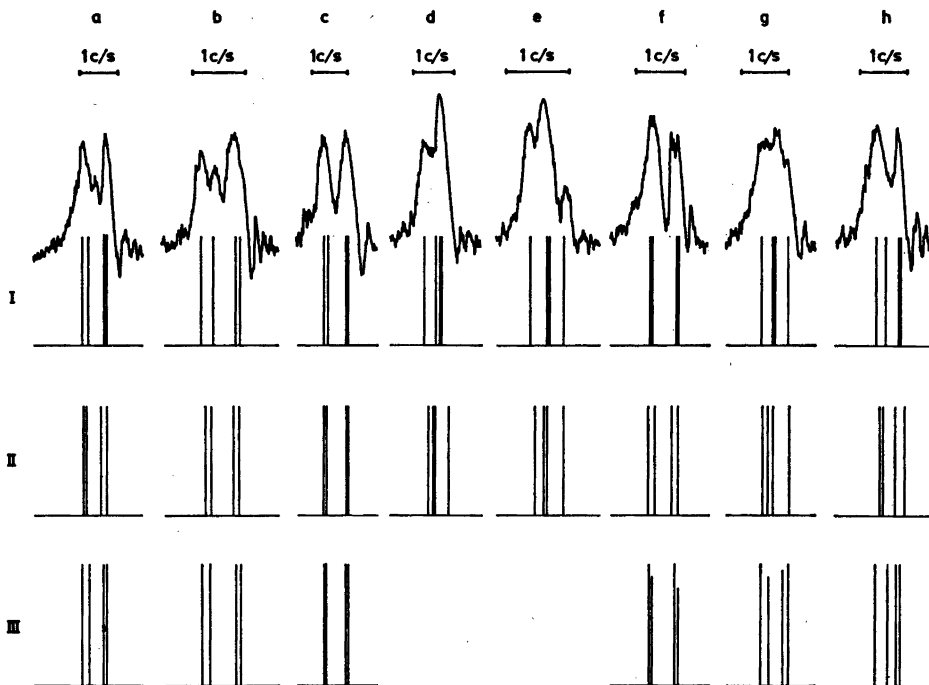
Fig. 8. Observed and predicted double resonance spectra of the CHO-part at various offsets with an rf. amplitude $\gamma H_2/2\pi = 2.0$ c/s. The offsets of the irradiating H_2 field are (in c/s): a) $+ 6.4$, b) $+ 5.5$, c) $+ 4.8$, d) $+ 0.2$, e) $- 0.4$, f) $- 5.3$, g) $- 6.0$, h) $- 6.6$. Sets (I) and (II) of the calculated spectra were obtained from Fig. 5 in a way analogous to Fig. 7 and correspond to the assumptions $J_{45} \times J_{CHO-5} > 0$ and $J_{45} \times J_{CHO-5} < 0$, respectively. Set (III) was obtained from Fig. 6 calculated by use of the pseudo-AX theory under the assumption $J_{45} \times J_{CHO-5} > 0$.

ed and observed spectra is obtained when J_{AB} and J_{BX} are assumed to carry the same sign. At the offset employed in recording the spectrum in Fig. 7 a, for example, one expects an enlargement of the splitting between lines X1 and X2 if the signs of J_{AB} and J_{BX} are equal but an enlargement of the splitting between the lines X3 and X4 if the two couplings carry opposite signs. The spectrum observed indicates that the separation between the lines X1 and X2 has increased while the separation between the lines X3 and X4 has remained constant, because the intensity of the highest field in the observed triplet is greater than that of the two low field lines. The observed intensity difference is smaller than that theoretically predicted but this phenomenon is to be expected since the highest field line in a closely spaced multiplet is normally depressed under the conditions used to obtain the present spectrum (*cf.* Fig. 7 d in which the lowest and highest field lines should theoretically have equal intensity).

In the second series of experiments (Fig. 8) which was carried out with a lower irradiating H_2 amplitude ($\gamma H_2/2\pi = 2.0$ c/s), a number of selective double irradiations as well as general double irradiation experiments were performed. Three sets of theoretical spectra are included in Fig. 8. The upmost row (I) was obtained from Fig. 5 by intersection of field sweep lines (a) — (h) with the double resonance transition curves and thus correspond to the assumption that $J_{AB} \times J_{BX} > 0$. The second row (II) corresponds to the assumption that $J_{AB} \times J_{BX} < 0$ and was obtained from Fig. 5 by reflection of the transition curves in the ordinate. The third row (III) corresponds to equal signs of J_{AB} and J_{BX} and was similarly obtained from Fig. 6, calculated by use of the pseudo-AX theory. The spectra in this series were obtained under somewhat better resolution than in the preceding series. Four of the spectra in Fig. 8 (a, b, d, and h) display obvious asymmetries from which one may deduce the relative signs of the coupling constants. It is seen that the first set of calculated spectra, in which J_{AB} and J_{BX} are assumed to carry the same sign (set I), is in excellent agreement with the observed spectra, whereas the spectra calculated for opposite signs of J_{AB} and J_{BX} (set II) deviate significantly from the observed ones depicted in Fig. 8 a, b, d, g, and h. Figs. 8 a and 8 b show a selective enlargement ("boosting") of the X1, X2 doublet splitting from an original value of 0.08 c/s to a maximum of 0.25 c/s in Fig. 8 b. The selectivity of the irradiation is illustrated by the fact that a change in offset of only 0.7 c/s from that of optimum "boosting" produces a virtually unperturbed spectrum (Fig. 8 c). The theoretical spectra of set III in Fig. 8 do not reproduce the experimental spectra in all cases (cf. especially III g and III h). The reason for these deviations is obviously that the assumptions of the pseudo-AX theory are not fully satisfied as discussed in section 4.1.

5. CONCLUSION

The present work shows that the selective enlargement technique may be used for the determination of the relative signs of spin couplings in three spin systems with one unresolved splitting. The largest "boosted" splitting attainable with selective irradiation of two lines ω_{rs} and ω_{pq} in a pseudo AX pair is for large values of H_2 given by $2\gamma H_2||\lambda_{pq}| - |\lambda_{rs}||$.[12] Consequently the selective enlargement technique can be used for the determination of relative signs only if the enlarged splitting can be resolved without using H_2 amplitudes so large as to perturb other lines in the spectrum as well. A sufficient criterion for selectivity is that the "boosted" splitting should revert towards the unperturbed pattern when the irradiating frequency ω_2 is moved away in either direction from the frequency of optimum boosting (cf. Fig. 8 a—c).

In cases when the selective boosting experiment may not be successfully performed one may aim at producing significant asymmetries in the X-band by strong non-selective irradiation in the AB band. A very characteristic asymmetry is the 1:3 "doublet" structure obtained when the strong irradiation is applied near the center of the AB-band (cf. Fig. 7 b and c and Fig. 8 d).

The result that J_{CHO-5} is of the same sign as J_{45} and thus presumably positive [25] while J_{CHO-4} is negative is in agreement with our earlier contention

that the sign of the side-chain couplings in thiophenealdehydes are the same as those in furanealdehydes.[10]

REFERENCES

1. Sternhell, S. *Rev. Pure and Appl. Chem.* **14** (1964) 15.
2. Hoffman, R. A. and Gronowitz, S. *Acta Chem. Scand.* **13** (1959) 1477.
3. Hoffman, R. A. and Gronowitz, S. *Arkiv Kemi* **16** (1960) 471.
4. Hoffman, R. A. and Gronowitz, S. *Arkiv Kemi* **16** (1960) 501.
5. Hoffman, R. A. and Gronowitz, S. *Arkiv Kemi* **16** (1960) 515.
6. Hoffman, R. A. *Arkiv Kemi* **17** (1960) 1.
7. Hoffman, R. A., Gestblom, B., Gronowitz, S. and Forsén, S. *J. Mol. Spectry.* **11** (1963) 454.
8. Forsén, S. and Hoffman, R. A. *Acta Chem. Scand.* **18** (1964) 249.
9. Hoffman, R. A., Gestblom, B. and Forsén, S. *J. Mol. Spectry.* **13** (1964) 221.
10. Forsén, S., Gestblom, B., Gronowitz, S. and Hoffman, R. A. *Acta Chem. Scand.* **18** (1964) 313.
11. Gestblom, B. and Mathiasson, B. *Acta Chem. Scand.* **18** (1964) 1905.
12. Hoffman, R. A., Forsén, S., Gestblom, B. and Rodmar, S. *J. Chem. Phys.* **42** (1965) 1695.
13. Gestblom, B., Gronowitz, S., Hoffman, R. A., Mathiasson, B. and Rodmar, S. *Arkiv Kemi* **23** (1965) 483.
14. Gestblom, B., Gronowitz, S., Hoffman, R. A., Mathiasson, B. and Rodmar, S. *Arkiv Kemi* **23** (1965) 501.
15. Gestblom, B., Gronowitz, S., Hoffman, R. A. and Mathiasson, B. *Arkiv Kemi* **23** (1965) 517.
16. Forsén, S. and Åkermark, B. *Acta Chem. Scand.* **17** (1963) 1712.
17. Forsén, S. and Åkermark, B. *Acta Chem. Scand. In press.*
18. Maher, J. P. and Evans, D. F. *Proc. Chem. Soc.* **1961** 208.
19. Freeman, R. and Whiffen, D. H. *Mol. Phys.* **4** (1961) 321.
20. Cohen, A. D., Freeman, R., Mc Lauchlan, K. A. and Whiffen, W.H. *Mol. Phys.* **7** (1963) 45.
21. Rao, B. D. N. and Baldeschwieler, J. D. *J. Chem. Phys.* **37** (1962) 2473.
22. Anderson, W. A. *Phys. Rev.* **102** (1956) 151.
23. Anderson, W. A. *NMR and EPR Spectroscopy,* New York 1960, p. 164.
24. Pople, J. A., Schneider, W. G. and Bernstein, H. J. *High-resolution nuclear magnetic resonance,* New York 1959.
25. Buckingham, A. P. and Mc Lauchlan, K. A. *Proc. Chem. Soc.* **1963** 144.