A Dynamic ^{1}H Nuclear Magnetic Resonance Spectral Study of 1,4-Dithian and of its Dihalogen Complexes

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The cyclic ligand 1,4-dithian, $C_4H_8S_2$, readily forms complexes with halogens and the ^{1}H n.m.r. spectra of these complexes and of 1,4-dithian itself have been studied over a wide temperature range. At low temperatures a coalescence phenomenon was observed in the spectrum of 1,4-dithian which has been attributed to the onset of rapid ring reversal occurring in the molecule. The AA'BB' spectrum observed below coalescence has been analysed and it proved possible to simulate the appearance of the spectrum over a temperature range by using n.m.r. band shape fitting techniques. A coalescence phenomenon was also observed in the spectra of the complexes $C_4H_8S_2,2Cl_2$ and $C_4H_8S_2,2Br_2$. This coalescence was found to be due not to reversal of the 1,4-dithian ring, but rather to inversion of configuration at the sulphur atoms. Thermodynamic activation parameters are reported for both ring reversal of 1,4-dithian and for inversion of configuration at the ligand atoms in the halogen complexes.

VARIABLE temperature n.m.r. spectroscopic studies have been attempted for a number of 1,4-disubstituted cyclohexane-type molecules. 1,4-Oxa-thian and -selenan have been shown to have the symmetric chair as their stable low temperature conformation; for the series of 1,4-oxachalcenans which includes 1,4-oxatelluran, the molecule becomes more flexible with the increasing size of the heavier chalcogen atom.[1,2] For the series of 1,4-dichalcenans, initial reports indicated that the ^{1}H n.m.r. spectra of neither 1,4-dioxan [3] nor 1,4-dithian [4] exhibited any apparent change with temperature, both remaining as singlets down to 169 K, thus suggesting that the barrier to their ring reversal is <34 kJ mol^{-1} However, a coalescence phenomenon has been recently reported to occur in the ^{13}C satellites of the ^{1}H n.m.r spectrum of 1,4-dioxan and it has been determined that the stable low temperature conformation of this molecule is the symmetric chair and that the free energy of activation for ring reversal at 179.5 K is 40.74 kJ mol^{-1}.[5] We have previously reported [6] that a coalescence phenomenon occurs in the ^{1}H n.m.r. spectrum of $CFCl_3$ solutions of 1,4-diselenan at 173 K although the spectrum below this temperature is insufficiently resolved to allow for spectral analysis. We now report that a coalescence phenomenon occurs in the ^{1}H n.m.r. spectra of solutions of 1,4-dithian in both $CFCl_3$ and CS_2 and have succeeded in performing full spectral analysis for the $CFCl_3$ solution of this molecule.

The sulphur atoms in 1,4-dithian can act as donors to halogens, and each sulphur atom can take up a molecule of halogen to give complexes of formula $C_4H_8S_2,2X_2$, where X is Cl, Br, or I. McCullough has reported [7] *X*-ray crystallographic studies for $C_4H_8S_2,2I_2$ and has shown that the heterocycle retains its 'normal' chair conformation. The bonding of the halogen molecules to the sulphur atoms is in the form I–I–S showing that the formal oxidation state of the sulphur atoms is +2 rather than +4. An oxidation state of +2 implies a tetrahedral arrangement of electron pairs about the sulphur atoms and a stereochemically active lone pair, whereas a +4 oxidation state would imply a trigonal bipyramidal arrangement of electron pairs and probably a stereochemically inactive lone pair. As part of our studies of ring reversal and configurational inversion processes occurring in sulphur- and selenium-containing complexes we also report band-shape fitting studies for the ^{1}H n.m.r. spectra of these dihalogen complexes.

RESULTS AND DISCUSSION

The solubility of 1,4-dithian in CS_2 falls rapidly with decreasing temperature but even with very dilute solutions a coalescence phenomenon is observed at *ca.* 205 K, thus contradicting the earlier report. However, in this solvent the spectrum below coalescence is insufficiently well resolved to permit analysis. In contrast, the low temperature 90 MHz ^{1}H n.m.r. spectrum of this compound in $CFCl_3$ solution is well resolved and is shown in Figure 1. It consists of an AA'BB' multiplet and spectral analysis obtained by means of the LAOCN3 program [8] yielded the following parameters: $\Delta\nu_{AB}$ 31.8; $J_{AB} = J_{A'B'} = -14.7$; $J_{BB'}$ 11.5; $J_{A'B} = J_{AB'} = 4.2$; $J_{AA'}$ 4.6 Hz. The geminal coupling constants are negative and typical of those for protons attached to sp^3 hybridised carbon atoms.

The pattern of one major and three minor vicinal coupling constants indicates that the stable low temperature conformation of this molecule is the symmetric chair.[1]

Warming the solution of 1,4-dithian produced a coalescence phenomenon and the singlet observed at room temperature emerged at temperatures above *ca.* 205 K. The coalescence phenomenon observed in the spectrum of 1,4-dithian is most reasonably explained

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[1] J. C. Barnes, G. Hunter, and M. W. Lown, *J.C.S. Perkin II*, 1975, 1354.

[2] F. R. Jenson and R. A. Neese, *J. Amer. Chem. Soc.*, 1975, **97**, 4922.

[3] E. Caspi, T. A. Wittstruck, and D. M. Diatak, *J. Org. Chem.*, 1962, **27**, 3183.

[4] F. Lautenschlager and G. F. Wright, *Canad. J. Chem.*, 1963, **41**, 1972.

[5] F. R. Jenson and R. A. Neese, *J. Amer. Chem. Soc.*, 1975, **97**, 4345.

[6] G. Hunter and R. C. Massey, *J.C.S. Dalton*, 1974, 1872.

[7] G. T. Chao and J. D. McCullough, *Acta Cryst.*, 1960, **13**, 727.

[8] A. A. Bothner-By and S. Castellano, Program 111, Quantum Chemistry Program Exchange, Chemistry Department, Indiana University.

in terms of ring reversal of the symmetric chair conformation. Lambert[9] and Buys[10,11] have developed the R value method whereby the ring dihedral angle ψ for the CH_2CH_2 fragment in six-membered rings may be calculated from the vicinal proton–proton coupling constants. For 1,4-dithian R has a value of 1.71 which corresponds to a value for ψ of 54.5°, indicating a flattening of the ring as compared with both cyclohexane (R 1.9, ψ 56°) and 1,4-dioxan (R 2.2, ψ 58°).[12]

Band shape analysis of the coalescence of the AA'BB' spectrum of 1,4-dithian was performed using the DNMR2 program,[13] and comparison of experimental and simulated spectra for varying temperatures and corresponding rate constants is shown in Figure 2. A good straight line Arrhenius plot was obtained and a value for the free energy of activation at 300 K in this molecule, $\Delta G_{300}^{\ddagger}$ 43.1 ± 1.5 kJ mol^{-1}, obtained.

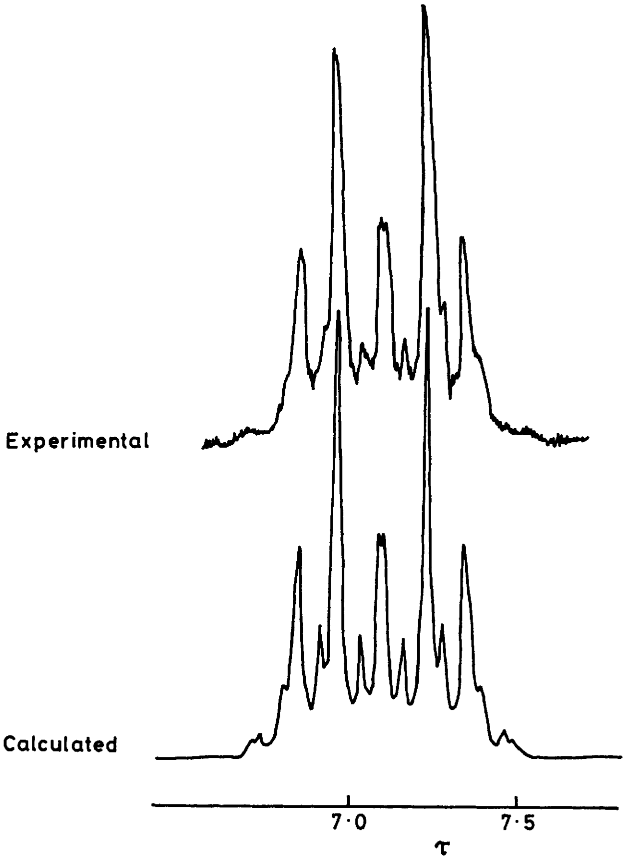

FIGURE 1 90 MHz ^1H N.m.r. spectrum of 1,4-dithian in $CFCl_3$ solution

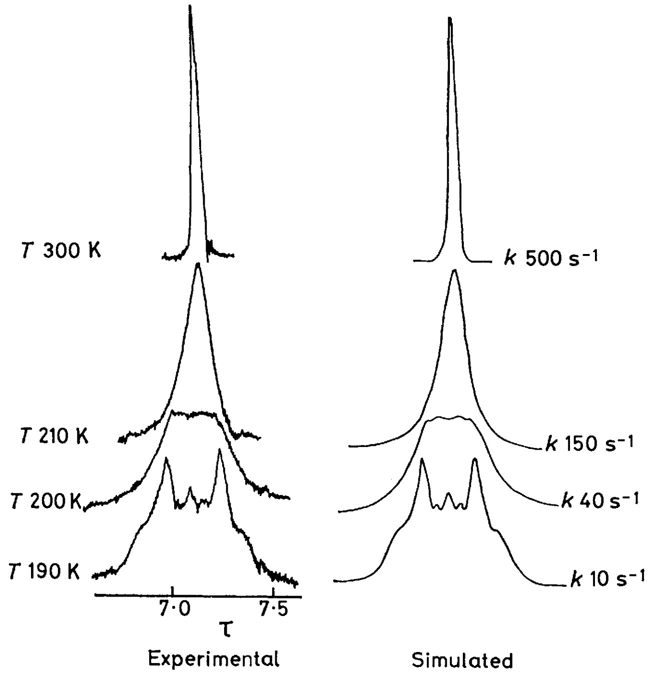

FIGURE 2 Comparison of experimental spectrum of 1,4-dithian in $CFCl_3$ solution and spectrum simulated on the basis of geminal proton exchange

For solutions of the halogen complexes, $C_4H_8S_2,2X_2$, where X = Cl, Br, or I, at temperatures much above ambient, the n.m.r. spectra consisted of singlets. Cooling solutions of the chlorine and bromine complexes produced a coalescence phenomenon in their spectra at *ca.* 315 and 195 K, respectively, whereas the spectrum of the iodine complex remained as a broadened singlet at 170 K. The coalescence phenomenon observed in the spectrum of the chlorine complex is almost certainly caused by a first-order process as the addition of either free 1,4-dithian or chlorine to solutions of the complex had little observable effect on the spectrum at temperatures in the region of coalescence. Similar experiments for the bromine complex were less successful as the chemical shifts of the complex and of 1,4-dithian are too similar to allow their spectra below coalescence to be separately observed and the addition of bromine to solutions of the complex reduced the latter's solubility to less than that required for adequate spectral resolution.

The spectra below coalescence for the chlorine and bromine complexes are shown in Figure 3 and were analysed without difficulty as AA'BB' multiplets and the following spectral parameters obtained: $C_4H_8S_2,2Cl_2$, $\Delta\nu_{AB}$ 67.7; $J_{AB} = J_{A'B'} = -14.4$; $J_{AA'}$ 12.0; $J_{AB'} = J_{A'B} = 3.1$; $J_{BB'}$ 4.1; $C_4H_8S_2,2Br_2$, $\Delta\nu_{AB}$ 27.9; $J_{AB} = J_{A'B'} = -14.5$; $J_{AA'}$ 10.2; $J_{AB'} = J_{A'B} = 1.9$; J_{BB} 1.4 Hz. It can be seen that $\Delta\nu_{AB}$ for $C_4H_8S_2,2Br_2$ is only about half that for $C_4H_8S_2,2Cl_2$ and it may be that the failure to observe a coalescence phenomenon in the spectrum of $C_4H_8S_2,2I_2$ is simply the result of a value for $\Delta\nu_{AB}$ too small to allow resolution of the AA'BB' multiplet.

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[9] J. B. Lambert, *Accounts Chem. Res.*, 1967, **4**, 82 and references therein.

[10] H. R. Buys, *Rec. Trav. chim.*, 1969, **88**, 1003.

[11] H. R. Buys, *Rec. Trav. chim.*, 1970, **84**, 1253.

[12] J. B. Lambert, *J. Amer. Chem. Soc.*, 1967, **89**, 1836.

[13] G. Binsch and D. A. Kleier, Program 140, Quantum Chemistry Program Exchange, Chemistry Department, Indiana University.

Interpretation of the coalescence phenomenon observed in the spectra of the complexes is more complicated than that for 1,4-dithian as there are now two intramolecular processes with different energy requirements which can conceivably occur in these molecules: (i) ring reversal of the flexible 1,4-dithian ligand; and (ii) inversion of configuration at a sulphur atom. As it is likely that the symmetric chair is by far the most energetically favoured conformation for the 1,4-dithian ring, the lone pairs of electrons on each sulphur atom can adopt either axial or equatorial positions to the ring. Therefore there are three configurations possible for these dihalogen complexes: with the halogens co-ordinated by equatorial lone pairs on both sulphur atoms (diequatorial complex); with the halogens co-ordinated by axial lone pairs on both sulphur atoms (diaxial complex); or with the halogens co-ordinated by an equatorial lone pair on one sulphur atom and by an axial lone pair on the other sulphur atom (equatorial-axial complex). The resulting four possible symmetric chair conformations and their reversed forms are shown in Figure 4. If these eight conformations are visualised as occupying the corners of a cube, the edges of which represent either ring reversal or configurational inversion at a single sulphur atom it can be seen that any pair of conformations can be interconverted either *via* the edges of the cube by a series of individual processes or *via* a diagonal by simultaneous combination of the processes along the corresponding edges.

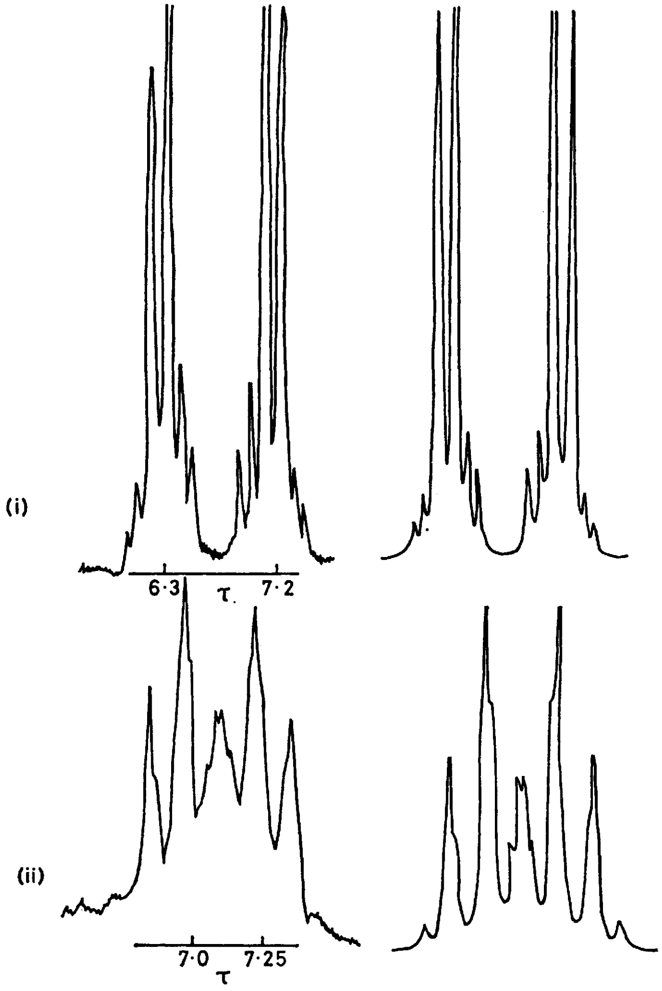

FIGURE 3 90 MHz ^{1}H N.m.r. low temperature spectra of (i) $C_4H_8S_2,2Cl_2$ in $CDCl_3$ at 270 K; (ii) $C_4H_8S_2,2Br_2$ in CD_2Cl_2 at 160 K

Neither ring reversal nor configurational inversion can, however, by themselves generate the observed high temperature A_4 spectrum as this requires a process by which a hydrogen atom in, say, an equatorial position on a given carbon atom can move to an axial position in an exactly equivalent conformation. For the chlorine complex the observed coalescence occurs at *ca.* 315 K, at which temperature ring reversal would already be very rapid so that the coalescence clearly indicates the onset of rapid configurational inversion at the sulphur atoms. Therefore the AA′BB′ spectrum observed below the coalescence temperature corresponds to a situation in which there is rapid ring reversal but slow configurational inversion. The spectral parameters of the AA′BB′ multiplet give an indication as to the stable low temperature configuration for the molecule. The axial-equatorial conformers (II), (III), (VI), and (VII) are of equal energy, equally populated, and have identical ^{1}H

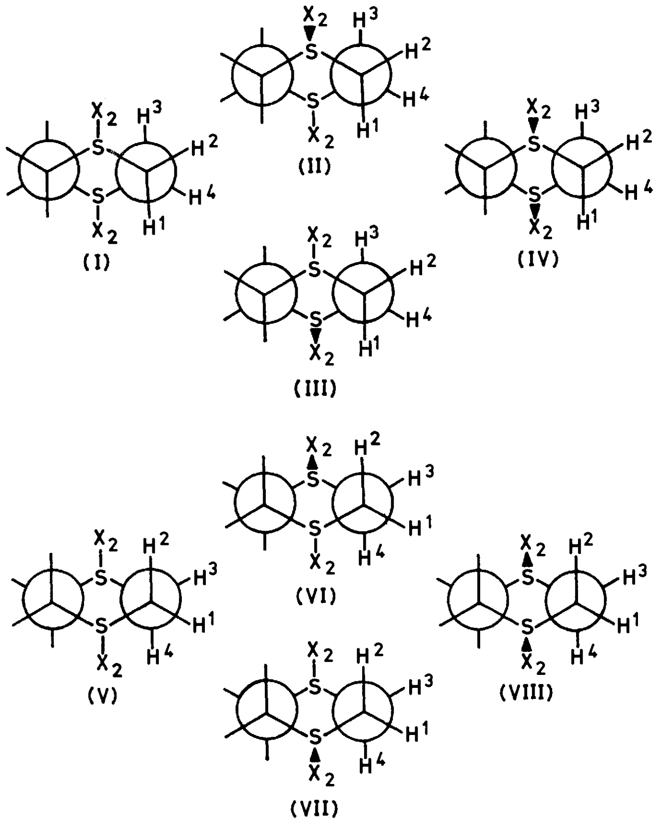

FIGURE 4 The four symmetric chair conformations and their reversed forms for $C_4H_8S_2,2X_2$

n.m.r. spectra. The four close-coupled protons of each of these conformers are chemically non-equivalent and slow ring reversal would give rise to an ABCD spectrum. Rapid ring reversal of, say, conformer (II) would give rise to a spectrum consisting of an AA'BB' multiplet with only two sets of vicinal coupling constants. The diequatorial pair of conformers, (I) and (V), are not energetically equivalent to the diaxial pair, (IV) and (VIII), and hence these pairs are unequally populated. Slow ring reversal of these conformers would give rise to a spectrum consisting of two overlapping AA'BB' multiplets of unequal intensity. Rapid ring reversal, leading to diequatorial $\rightleftharpoons$ diaxial interconversion, say conformer (I) $\rightleftharpoons$ conformer (VIII), would give rise to a single AA'BB' multiplet with all the vicinal coupling constants of different magnitude, although a pattern of one major and three minor values would be expected. This is, of course, the observed pattern of spectral parameters and shows that the interconversion of diequatorial to diaxial rather than of axial–equatorial to equatorial–axial conformers is occurring. Because $J_{AA'}$ is so much larger than $J_{BB'}$ there must be a very large population imbalance between the diaxial and diequatorial configurations although it is impossible to be specific as to which is the more favoured. Indeed the value for $J_{AA'}$ is almost as large as might be expected for the population of one configuration to be almost 100%. Therefore the lack of observance of a second, low temperature, coalescence phenomenon corresponding to the onset of slow ring reversal, and below which would be observed two AA'BB' multiplets of unequal intensity, is not surprising as the lower intensity multiplet would be overlapped by its more dominant partner whose appearance would be very little changed from that of the time-averaged AA'BB' multiplet resulting from rapid ring reversal.

The situation of rapid ring reversal combined with slow configurational inversion probably also applies below the observed coalescence for the bromine complex, although at this temperature (195 K) ring reversal would also be expected to be slow. Once again, however, the pattern of one major and three minor vicinal coupling constants for the AA'BB' multiplet shows that interconversion of axial–axial to equatorial–equatorial rather than of axial–equatorial to equatorial–axial conformers is occurring.

Band-shape fitting studies of the coalescence were carried out and comparison of experimental and simulated spectra for the bromine complex is shown in Figure 5. Values for the free energies of activation at 300 K were obtained for these molecules: $C_4H_8S_2,2Cl_2$, $\Delta G_{300}^{\ddagger}$ 64.0 ± 0.7; $C_4H_8S_2,2Br_2$, $\Delta G_{300}^{\ddagger}$ 47.1 ± 0.9 kJ mol^{-1}. The coalescence observed in the spectrum of the chlorine complex can be assigned without hesitation to the onset of rapid configurational inversion at the sulphur atoms. In the case of the bromine complex, ring reversal and configurational inversion at the sulphur atoms would appear to be of very similar energies and it is not possible to determine which process is responsible for the coalescence. However, the collapse of the AA'BB' multiplet to an A_4 singlet shows that both processes must have become rapid on the n.m.r. time scale and the value of $\Delta G_{300}^{\ddagger}$ recorded for this complex is therefore the maximum possible for configurational inversion. There is therefore a large difference in the energy requirements for configurational inversion at the sulphur atoms of the chlorine and bromine complexes.

There are a number of possible mechanisms by which inversion of configuration at a ligand atom can take place but perhaps the most plausible is that in which in the transition state the lone pair possesses pure *p* character, with the bonds being sp^2 hybridised. This mechanism fits in well with the observation that the barrier to inversion about sulphur or selenium is lowered when bonded to a second or third row transition metal as the $(p\text{–}d)\pi$ overlap might well reduce the energy of the transition state. It may well be that in the case of the dihalogen complexes of 1,4-dithian there is more multiple bonding between sulphur and bromine than between sulphur and chlorine, thus making the transition state more accessible and lowering the barrier to inversion in the dibromine complex.

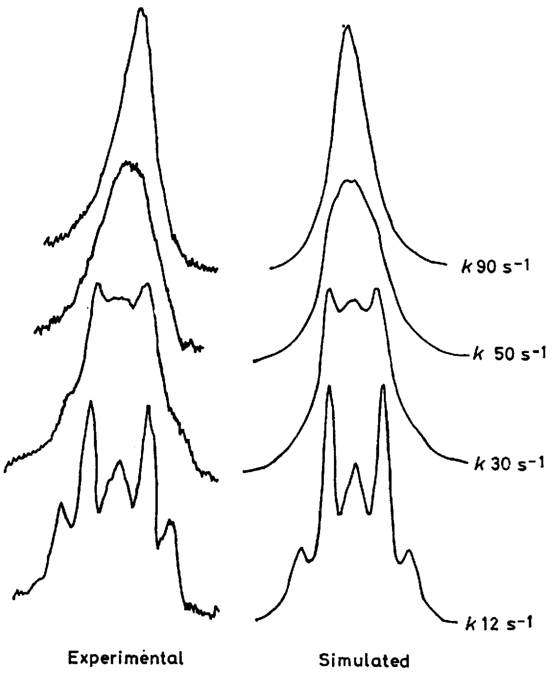

FIGURE 5 Comparison of experimental spectrum of $C_4H_8S_2,2Br_2$ in CD_2Cl_2 solution and spectrum simulated on the basis of geminal proton exchange

EXPERIMENTAL

1,4-*Dithian*.—1,4-Dithian was prepared and purified using published procedures.[14]

Dihalogen Complexes.—These were prepared by directly treating solutions of 1,4-dithian in carbon tetrachloride with the appropriate halogen. The dichlorine complex was initially obtained as an oil when the solvent was evaporated off. This was purified by column chromatography, using

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[14] R. G. Gillis and A. B. Lacey, *Org. Synth.*, 1959, **39**, 23.

silica as adsorbent and a mixture of carbon tetrachloride and light petroleum as eluant. The complex was obtained as crystals after evaporation of the solvent. The dibromine and di-iodine complexes were obtained as crystalline precipitates which were purified by recrystallisation from chloroform (Found: C, 18.4; H, 2.8. $C_4H_8Cl_4S_2$ requires C, 18.3; H, 3.1%. Found: C, 10.8; H, 1.9. $C_4H_8Br_4S_2$ requires C, 10.9; H, 1.8%. Found: C, 7.8; H, 1.5. $C_4H_8I_4S_2$ requires C, 7.6; H, 1.3%).

N.m.r. Spectra.—All spectra were obtained using a Bruker HX90 spectrometer fitted with a variable temperature probe. Temperatures were measured with a thermocouple mounted in the probe which was found to be accurate to ±1° by calibration with methanol and ethylene glycol using the formulae of Van Geet.[15]

Kinetic Analysis.—In the temperature regions of slow and intermediate exchange behaviour the spectra were recorded at 5° intervals and several times at each temperature. Simulated spectra were calculated by total lineshape analysis using the DNMR2 program.[13]

One of us (M. S.) thanks the Iranian Government for the award of a research scholarship.

[7/1514 *Received*, 22*nd August*, 1977]

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[15] A. L. Van Geet, *Analyt. Chem.*, 1968, **40**, 2227.