A Dynamic Nuclear Magnetic Resonance Study of Ring Inversion occurring in 1,4-Oxa-thian, -selenan, and -telluran

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The low temperature ^{1}H n.m.r. spectra of 1,4-oxachalcenans have been observed and for 1,4-oxathian and 1,4-oxaselenan consist of ABCD multiplets which have been analysed and for which spectral parameters are reported. Coalescence phenomena observed in the spectra were interpreted in terms of ring inversion occurring in the molecules and thermodynamic parameters obtained by means of total line-shape fitting techniques are reported for this process.

THE occurrence of ring inversion in the heterocyclic analogues of cyclohexane has excited considerable recent interest.[1] However, although temperature-dependent n.m.r. spectral studies have been reported for a variety of these heterocycles, few have been based on total line-shape fitting techniques and the majority of the reported thermodynamic parameters are probably of questionable value. We have an interest in the potential role of 1,4-oxachalcenans as ambidentate ligands and as background to this work have found it necessary to carry out temperature-dependent n.m.r. spectral studies for these compounds for which we report spectral analyses and thermodynamic parameters obtained from total line-shape fitting techniques.

RESULTS AND DISCUSSION

The room temperature 90 MHz ^{1}H n.m.r. spectrum for 1,4-oxa-thian, -selenan, and -telluran, consisted of a symmetrical AA'BB' multiplet with the absorptions attributable to the protons of the methylene group attached to the oxygen atom appearing downfield from those of the methylene group attached to the heavier chalcogen atom. Spectral analyses obtained by means of the LAOCOON 3 program[2] yield the parameters recorded in Table 1. The parameters obtained for 1,4-

TABLE 1

Parameters for the room temperature 90 MHz n.m.r. spectra of the 1,4-oxachalcenans

	Hz				
	$\Delta\nu_{AB}$	J_{trans}	J_{cis}	R	ψ (°)
1,4-Oxathian	115.0	7.21	2.72	2.65	61
1,4-Oxaselenan	123.0	7.22	2.74	2.64	61
1,4-Oxatelluran	122.0	7.55	2.99	2.59	60.5

oxathian confirm those quoted by Lambert,[3] which were recalculated from an initial report by Smith and Shoulders[4] of the spectrum of this compound at 60 MHz.

Cooling a $CFCl_3$ solution of 1,4-oxatelluran to 155 K only broadened the AA'BB' spectrum. Cooling similar solutions of 1,4-oxa-thian and -selenan produced coalescence phenomena and unsymmetrical ABCD spectra emerged at low temperature. The low temperature spectrum of 1,4-oxathian is illustrated in Figure 2. Unfortunately, this spectrum could not be further resolved

as viscosity broadening effects became important below ca. 155 K causing the overlap of closely separated peaks. However, the positions of many unresolved peaks could
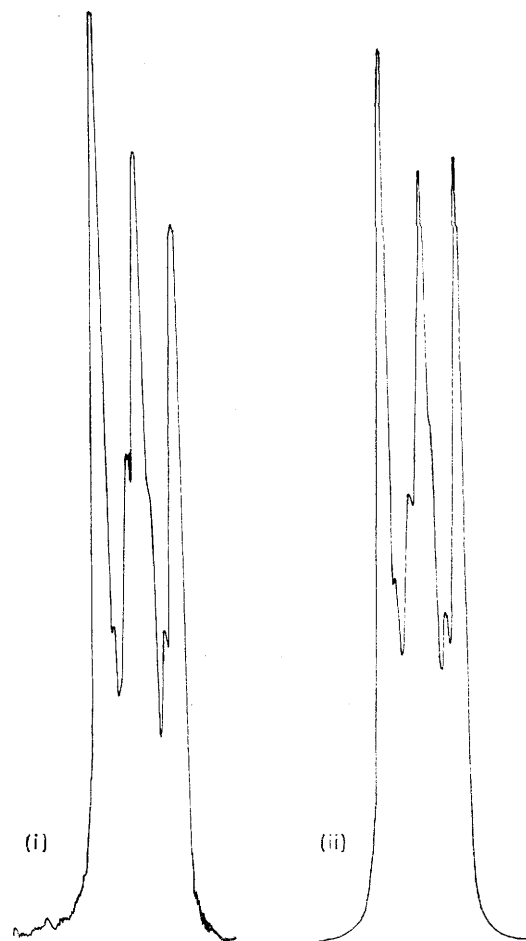

FIGURE 1 Experimental (i) and simulated (ii) S-methylene multiplet of 1,4-oxathian in $CFCl_3$ solution determined at 295 K and 90 MHz

be inferred from the appearance of shoulders on the major absorptions. Spectral analyses were once again performed by means of the LAOCOON 3 program and the only parameters which adequately reproduced these ABCD spectra are recorded in Table 2.

The relationship between vicinal proton couplings and

[1] See e.g., I. O. Sutherland, Ann. Reports N.M.R. Spectroscopy, 1971, 4, 109.
[2] A. A. Bothner-By and S. Castellano, Program III, Quantum Chemistry Program Exchange, Chemistry Department, Indiana University.
[3] J. B. Lambert, J. Amer. Chem. Soc., 1967, 89, 1836.
[4] W. B. Smith and B. A. Shoulders, J. Phys. Chem., 1965, 69, 579.

the H–C–C–H dihedral angle is given by a Karplus equation of the type (1) where ϕ is the dihedral angle and A and

$$J = A \cos^2\phi + n \cos\phi \qquad (1)$$

n are constants whose values are sensitive to factors including the electronegativities of the other substituents
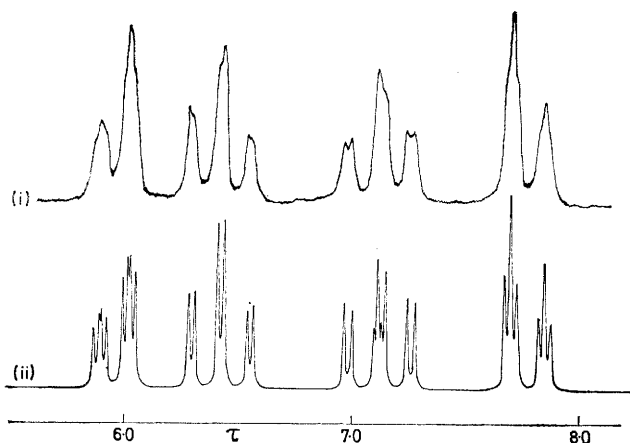

FIGURE 2 Experimental (i) and simulated (ii) 90 MHz ^{1}H n.m.r. spectrum of 1,4-oxathian in CFCl$_3$ solution at 155 K

on the carbon atoms. Whatever the actual values for these constants, dihedral angles approaching 0 and 180° should give rise to the largest vicinal coupling constants. From the pattern of one major and three minor vicinal coupling constants (Table 2) it is apparent that the stable, low-temperature form of these molecules is probably the

time-averaged spectra with two vicinal coupling constants equal in magnitude to $(J_{ax-ax} + J_{eq-eq})/2$ and $(J_{ax-eq} + J_{eq-ax})/2$. The values for these averaged vicinal coupling constants agree well with the vicinal coupling constants obtained from the analyses of the AA'BB' spectra observed at room temperature.

Lambert [5] and Buys [6,7] have developed the ' R value ' method whereby the ring dihedral angle ψ for the –CH$_2$–CH$_2$– fragments in six-membered rings may be calculated from the vicinal proton-proton coupling constants using equation (2). Defined in this way R is independent of the

$$R = J_{trans}/J_{cis} = (J_{ax-ax} + J_{eq-eq})/(J_{ax-eq} + J_{eq-ax}) = (3 - 2\cos^2\psi)/(4\cos^2\psi) \qquad (2)$$

electronegativity of substituents even though the individual couplings may be strongly dependent on the nature of the substituents.

It was found that for the ideal chair forms R would have a value of 1.9—2.2, for ' puckered ' chairs it would be >2.5, and for ' flattened ' chairs or flexible forms (various boat forms) R would be <1.8. For the 1,4-oxachalcenans R has a value ranging from 2.64 for 1,4-oxathian to 2.59 for 1,4-oxatelluran. These values correspond to a value for ψ of 61—62°, indicating a very slight amount of ring puckering compared with 1,4-dioxan (R 2.20, ψ ca. 58°).[3] It would appear that changes in the C–X–C fragment geometry as a consequence of increasing bond length in the series C–O < C–S < C–Se $\leqslant$ C–Te are not reflected to any great extent by changes in the geometry of the –CH$_2$–CH$_2$– system.

Line-shape fitting studies of the coalescence of the

TABLE 2

Data for the low temperature 90 MHz n.m.r. spectra of 1,4-oxa-thian and -selenan

	τ				J/Hz							
	$H_{eq}(O)$	$H_{ax}(O)$	$H_{ax}(X)$	$H_{eq}(X)$	$J_{gem(OCH_2)}$	$J_{gem(XCH_2)}$	$J_{eq(O),ax(X)}$	$J_{ax(O),eq(X)}$	$J_{eq(O),eq(X)}$	$J_{ax(O),ax(X)}$	J_{trans}	J_{cis}
1,4-Oxathian	5.968	6.428	7.133	7.778	−11.8	−13.5	3.1	2.3	2.1	12.1	7.1	2.7
1,4-Oxaselenan	5.833	6.354	7.058	7.821	−11.8	−13.1	2.8	2.6	1.7	12.3	7.0	2.7

symmetric chair as in this case only one dihedral angle can approach 180° and the other three should be ca. 60°. A symmetric, oxygen–chalcogen prow-boat conformation, where two dihedral angles should approach 0° would require a pattern consisting of two major and two minor vicinal coupling constants. The major vicinal coupling constant corresponds to J_{ax-ax} and identifies the axial proton absorptions. It is of interest to note that the absorption for the axial proton of the methylene group attached to the chalcogen atom is downfield from that of its geminal partner whereas the opposite situation applies to the absorptions for the protons of the methylene group attached to the oxygen atom.

The coalescence phenomena observed in the spectra of 1,4-oxa-thian and -selenan are most reasonably interpreted in terms of ring inversion in the molecules and rapid ring inversion should result in the appearance of

ABCD spectra were performed using the DNMR 2 program of Binsch and Kleier.[8] Comparisons of experimental and simulated spectra for 1,4-oxathian at various temperatures and corresponding rate constants are illustrated in Figure 3. For both compounds, good straight line Arrhenius plots were obtained over the temperature range 155—220 K and thermodynamic parameters obtained from these plots are recorded in Table 3. Errors quoted in Table 3 were assessed by considering the maximum and minimum slopes of the Arrhenius plots obtained when allowing for errors in temperature measurement of $\pm$ 1.0 K and in the rate constant sufficiently great that the simulated spectrum just no longer resembled the experimental spectrum.

It can be immediately inferred from the thermodynamic parameters for 1,4-oxa-thian and -selenan and from the non-appearance of coalescence phenomena in the spectra of 1,4-oxatelluran down to 155 K that increasing

[5] J. B. Lambert, Accounts Chem. Res., 1967, 4, 82, and references therein.
[6] H. R. Buys, Rec. Trav. chim., 1969, 88, 1003.
[7] H. R. Buys, Rec. Trav. chim., 1970, 89, 1253.

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

the carbon–heavier chalcogen bond length increases the flexibility of the molecule. One effect of increasing
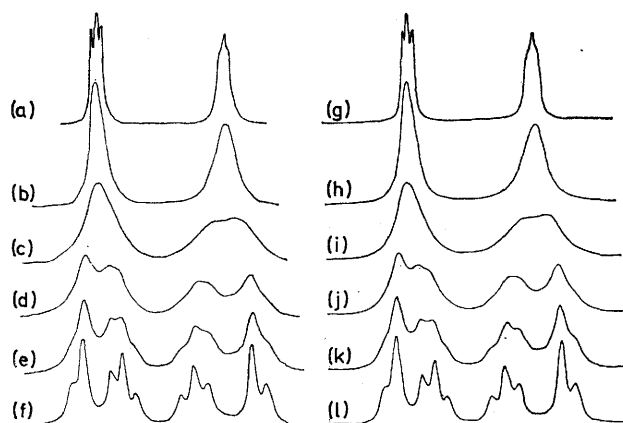

FIGURE 3 Comparison of experimental and simulated spectra for 1,4-oxathian: T/K (a) 215; (b) 200; (c) 190; (d) 185; (e) 180; (f) 175; k/s^{-1} (g) 1200; (h) 280; (i) 123; (j) 62; (k) 44; (l) 22

TABLE 3

Thermodynamic parameters for ring inversion occurring in 1,4-oxa-thian and -selenan

	$E_a/$ kJ mol^{-1}	$\Delta H_{300}^{\ddagger}/$ kJ mol^{-1}	$\Delta G_{300}^{\ddagger}/$ kJ mol^{-1}	$\Delta S^{\ddagger}/$ J mol^{-1} K^{-1}
1,4-Oxathian	30.9	28.4	46.0	−50.0
	±1.7	±1.7	±1.3	±13.0
1,4-Oxaselenan	25.1	22.6	42.6	−67.0
	±1.7	±1.7	±1.3	±13.0

this bond length would be to reduce non-bonding interactions between the two lone pairs on the heavier chalcogen atom and the two protons on the adjacent carbon.

The inversion process for the symmetric chain conformation of cyclohexane is generally believed to involve one of six possible twist-chair transition states. The statis-
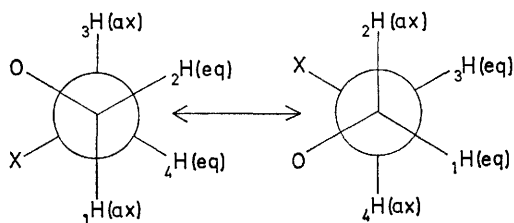

FIGURE 4 Newman projection along a C=C bond of ring inversion in 1,4-oxachalcenans

tics of the interconversion are consistent with a positive entropy of activation of magnitude $R\ln6$ as there are six degenerate pathways available for the process chair ⟶ twist-chair. In the case of the 1,4-oxachalcenans not all the twist-chair conformations are of equal energy but even so, a similar inversion process to that of cyclohexane would, on purely statistical grounds, still be expected to give rise to a small, positive value for $\Delta S_{cc}^{\ddagger}$.

Although the experimental $\Delta S^{\ddagger}$ values are likely to be considerably less accurate than the other parameters, even allowing for the maximum error, it can be seen that

this parameter is substantial and negative. This is somewhat surprising as it implies that the transition state is more symmetrical and rigidly defined than the ground state, and perhaps suggests that for these compounds it is not a twist-chair conformation. However, in the absence of relevant molecular mechanics calculations it would be unwise to speculate further as to the nature of this transition state.
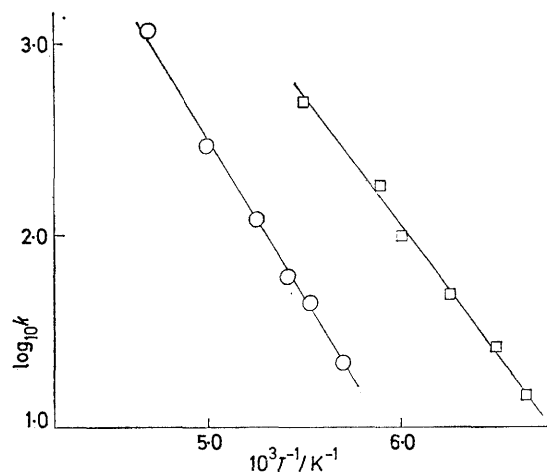

FIGURE 5 Arrhenius plots for 1,4-oxathian (◯) and 1,4-oxaselenan (☐)

EXPERIMENTAL

1,4-Oxachalcenans.—1,4-Oxathian was supplied by the Aldrich. 1,4-Oxa-selenan and -telluran were prepared and purified by published procedures.[9,10]

N.m.r. Spectra.—All spectra were obtained using a Bruker HX90 spectrometer equipped 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 using the formulae of Van Geet.[11]

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 line-shape analysis using the DNMR2 program.[8] Amongst other parameters this program requires the line widths in the absence of exchange and these were obtained by observation of the signal for the tetramethylsilane used as internal standard. It was found that outside the regions of very slow or very fast exchange, neither of which were used in the actual kinetic analysis, the simulated spectra, although very sensitive to changes in the value of the rate constant, were relatively insensitive to changes in the value for the line width in the absence of exchange. The dynamic processes were treated as ABCD ⇌ BADC exchanging systems. Simulated and experimental spectra were fitted by visual comparison.

[9] J. D. McCullough and A. Lefohn, Inorg. Chem., 1966, 5, 150.

[10] C. S. Gibson and J. D. A. Johnson, J. Chem. Soc., 1931, 266.
[11] A. L. Van Geet, Analyt. Chem., 1968, 40, 2227.