

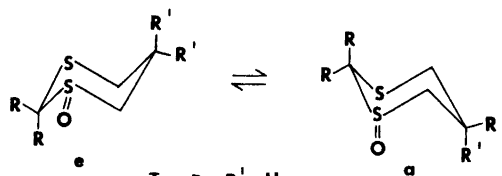
$\text{Ca}(\text{D-CDTA})^{2-}$  possesses a structure of its own, since the effects observed were very small.

It is difficult to explain how the ammonium ion influences step  $1 \rightarrow 2$  in the stated mechanism. It seems reasonable though to assume that this step is very complex consisting perhaps of several steps where an intermediate such as  $\text{M}'\text{NH}_4\text{CDTA}$  is found in one of the steps.

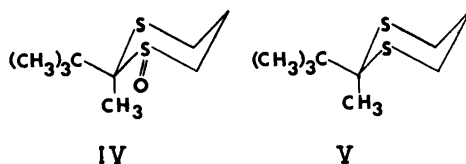
It is necessary to control the factors that affect the reaction rates when making use of the kinetic properties of the CDTA complexes of the alkaline earth ions in analytical chemistry.<sup>2</sup> The present investigation has shown that  $[\text{NH}_4^+]$  has such pronounced influence on the values of  $k_d$  that a prior knowledge of  $[\text{NH}_4^+]$  in the sample to be analysed is essential for the method. Further studies<sup>6</sup> on the differential kinetic analysis of the alkaline earth ions are being carried out with particular emphasis on the use of classical spectrophotometry in automated analyses.

1. Margerum, D. W., Menardi, P. J. and Janes, D. L. *Inorg. Chem.* 6 (1967) 283.
2. Pausch, J. B. and Margerum, D. W. *Anal. Chem.* 41 (1969) 226.
3. Jensen, A. and Larsen, N. R. *Acta Chem. Scand.* 27 (1973) 1838.
4. Larsen, N. R. and Jensen, A. *Acta Chem. Scand. A* 28 (1974) 638.
5. Carr, J. D. and Schwartzfager, D. G. *J. Am. Chem. Soc.* 97 (1975) 315.
6. Dahl, J. H. and Jensen, A. *To be published.*

Received March 18, 1976.



- I  $R = R' = \text{H}$   
 II  $R = \text{Me}, R' = \text{H}$   
 III  $R = \text{H}, R' = \text{O}$



equatorial site. In contrast thiane 1-oxide,<sup>6</sup> 1,3-oxathiane 3-oxide,<sup>4,7</sup> and thiane-3-one 1-oxide<sup>3</sup> adopt preferentially the axial  $\text{S}=\text{O}$  conformer. The origin of the equatorial  $\text{S}=\text{O}$  preference in I–III is somewhat unclear but a suggestion<sup>1</sup> that dipolar interactions are involved has recently received support in the form of force field calculations performed by Allinger and Kao.<sup>8</sup> These workers also calculated that conformer 1e is 4.2 kcal mol<sup>-1</sup> more stable than the lowest energy twist form.

In the present paper we report the analysis of the 100 MHz spectrum of the 2-*t*-butyl-2-

Table 1. 100 MHz spectral parameters (in Hz) of IV and V in  $\text{CDCl}_3$ .

	Chemical shift <sup>a</sup>		Coupling constants		
	IV	V <sup>b</sup>	IV		V <sup>b</sup>
4a	266.60	303.11	4a5a	12.75	11.85
4e	239.38	271.80	4e5e	3.00	4.35
5a	215.07	178.73	4a5e	2.92	3.28
5e	228.88	205.47	4e5a	3.97	3.96
6a	267.13	303.11	5a6a	14.21	11.85
6e	301.85	271.80	5e6e	3.82	4.35
			5a6e	3.39	3.96
			5e6a	3.23	3.28
			4a4e	-14.49	-14.46
			5a5e	-14.54	-13.56
			6a6e	-13.31	-14.46
			4e6e	1.57	0.65
			4a6a	-0.18	0.03
			4a6e	-0.23	-0.05
			4e6a	-0.41	-0.05

<sup>a</sup> Downfield from TMS. <sup>b</sup> Data taken from Ref. 11.

### Analysis of the 100 MHz <sup>1</sup>H NMR Spectrum and Conformation of *trans*-2-*t*-Butyl-*cis*-2-methyl-1,3-dithiane 1-Oxide

KNUT BERGESEN,<sup>a</sup> MICHAEL J. COOK<sup>b</sup> and ALAN P. TONGE<sup>b</sup>

<sup>a</sup> Department of Chemistry, University of Bergen, Allégatan 70, N-5014 Bergen-Univ., Norway and <sup>b</sup> School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, England

Recent studies from our laboratories<sup>1–3</sup> and elsewhere<sup>4,5</sup> have demonstrated that the  $\text{S}=\text{O}$  bond of 1,3-dithiane 1-oxides I, II, III favours the

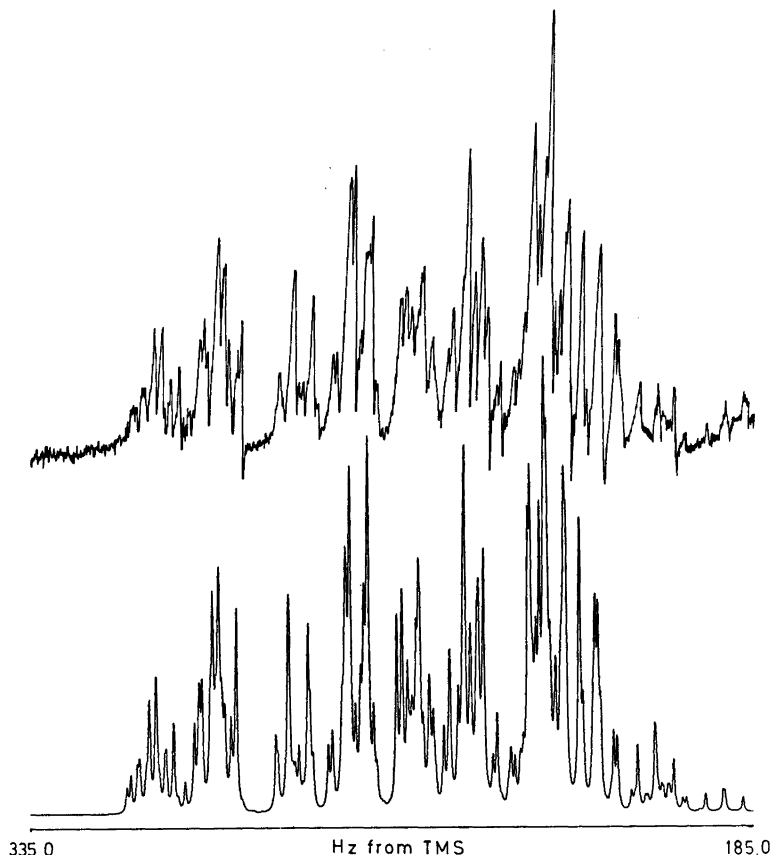


Fig. 1. Experimental (upper trace) and calculated (lower trace) 100 MHz spectrum of *trans*-2-*t*-butyl-*cis*-2-methyl-1,3-dithiane 1-oxide.

methyl derivative IV. Earlier we used<sup>1,2</sup> this compound as a "fixed chair" model in investigations of conformational equilibria of mobile 1,3-dithiane 1-oxides, but our present interest lay in a closer appraisal of its ring shape. The spectrum, Fig. 1, was analysed as an ABCDEF system using the LAOCN 3 program.<sup>9</sup> Input parameters were chosen largely on the basis of data obtained earlier from a crude first order analysis of the 220 MHz spectrum.<sup>2</sup> All parameters were allowed to vary and the values at the final iteration are reported in Table 1. The r.m.s. error of fit of 129 experimental and calculated transitions was 0.083. The calculated "probable error" for each parameter was 0.03 or less. The real errors are expected to be 2.5 times this value.<sup>10</sup> We find that the data obtained from the 220 MHz spectrum<sup>2</sup> are in moderately good agreement with the refined data obtained here.

Recently we reported<sup>11</sup> the analysis of the spectrum of 2-*t*-butyl-2-methyl-1,3-dithiane, V,

and the data are reproduced here to facilitate comparison. H-5a, H-5e, and H-6e are deshielded in IV relative to V but H-6a and the protons H-4a and H-4e, which are rather distant from the S=O bond, are significantly more shielded.  ${}^2J_{4,4}$  is much the same in both IV and V but  ${}^2J_{5,5}$  is smaller (more negative) and  ${}^2J_{4,6}$  larger in the former. The vicinal coupling constants are generally typical of those expected for rings "locked" in chair type conformations. However, there are small but significant variations in corresponding vicinal couplings between protons on C-4 and C-5, and on C-5 and C-6 in IV and these differ again from those in V. Such variations may arise from different internal dihedral angles,  $\Psi$ , within the rings as well as from different electronegativities of sulfide and sulfoxide sulfur atoms. The Lambert-Buys *R*-value method<sup>12</sup> provides a means of estimating  $\Psi$  from *R*, the ratio  $\sum^3 J_{\text{trans}} / \sum^3 J_{\text{cis}}$ , using the equation  $\cos \Psi = 3/(2 + 4R)^{\frac{1}{2}}$ . In this approach

electronegativity effects cancel, at least to a first approximation. By this treatment  $\Psi_{6s}$  and  $\Psi_{4s}$  in IV are 59 and 61°, respectively, so demonstrating that the  $\text{CH}_2-\text{CH}_2$  fragment adjacent to the sulfoxide group is the more puckered. The ring is also marginally more puckered than V in this region ( $\Psi = 58^\circ$ ). The latter value, which is 5° lower than that in 2-phenyl-1,3-dithiane, we earlier interpreted in terms of flattening due to the axial 2-methyl group and/or the presence of twist forms.<sup>11</sup> It seems likely that similar effects occur in IV also.

*Experimental, trans-2-t-Butyl-cis-2-methyl-1,3-dithiane 1-oxide IV* was prepared as described in Ref. 2.

The NMR spectrum was recorded of a 10 % solution in  $\text{CDCl}_3$  using a 100 MHz Varian HA-100 spectrometer operating at 35°. Line positions were taken by averaging data from four 100 Hz sweepwidth spectra, calibrated at every 10 Hz. Spectral analysis was performed using a local version of the LAOCN3 program and carried out on a UNIVAC 1110 computer. Graphical presentation of data, Fig. 1, was obtained using a CALCOMP plotter.

*Acknowledgement.* We thank NATO for providing a research grant to MJC and KB.

1. Cook, M. J. and Tonge, A. P. *Tetrahedron Lett.* (1973) 849.
2. Cook, M. J. and Tonge, A. P. *J. Chem. Soc. Perkin Trans. 2* (1976) 767.
3. Bergesen, K., Carden, B. M. and Cook, M. J. *Tetrahedron Lett.* (1975) 4479.
4. Van Acker, L. and Anteunis, M. *Tetrahedron Lett.* (1974) 225.
5. Khan, S. A., Lambert, J. B., Hernandez, O. and Carey, F. A. *J. Am. Chem. Soc.* 97 (1975) 1468.
6. Lambert, J. B. and Keske, R. G. *J. Org. Chem.* 31 (1966) 3429.
7. Bergesen, K., Cook, M. J. and Tonge, A. P. *Org. Magn. Reson.* 6 (1974) 127.
8. Allinger, N. L. and Kao, J. *Tetrahedron* 32 (1976) 529.
9. Castellano, S. and Bothner-By, A. A. *J. Phys. Chem.* 41 (1964) 3863.
10. Ewing, D. F. *Org. Magn. Reson.* 7 (1975) 520.
11. Bergesen, K., Carden, B. M. and Cook, M. J. *J. Chem. Soc. Perkin Trans. 2* (1976) 365.
12. For a review see Lambert, J. B. *Acc. Chem. Res.* 4 (1971) 87.

Received May 6, 1976

## Stability Constants for Scandium Thiodiacetate Complexes

INGEMAR DELLIN

Physical Chemistry I, Chemical Center, P.O.B. 740, S-220 07 Lund 7, Sweden

Thermodynamic data such as  $\Delta G_f^\circ$ ,  $\Delta H_f^\circ$ , and  $\Delta S_f^\circ$  for complex formation reactions in aqueous solution between lanthanoid(III) ions and carboxylate ligands show that these thermodynamic properties are greatly affected by the geometrical requirements of the ligand and the size of the metal ion. As scandium(III) has a similar electron configuration as the lanthanoids but is considerably smaller (the radii of the lanthanoid ions are in the range 1.06–0.85 Å, while that of  $\text{Sc}^{3+}$  is 0.73 Å<sup>1</sup>), data on scandium complexes should give additional information on the effects of a variation of the metal ion radius upon the thermodynamic characteristics of complex formation.

The earlier measurements on some lanthanoid thiodiacetate complexes<sup>2</sup> have here been extended to the scandium thiodiacetate system. The main reasons for this investigation are summarized below:

i. For the scandium complexes, the ratio between the consecutive formation constants,  $K_1/K_2$ , is low for the bidentate ligands malonate<sup>3</sup> and oxalate<sup>4</sup> ( $\approx 40$ ), but quite high ( $\approx 10^4$ ) for terdentate ligands such as oxydiacetate<sup>5</sup> and dipicolinate.<sup>3</sup> The lanthanoids are typical hard acids which ought to form poor bonds with sulfur donors. The results obtained from the lanthanoid thiodiacetate systems confirms this expectation, i.e. the ligand seems to be effectively bidentate.<sup>2</sup> A determination of  $K_1/K_2$  for the scandium thiodiacetate complexes will indicate how the ligand is bonded.

ii. The stability of acid complexes as  $\text{MHA}^{2+}$  also gives information on the bonding in and the geometry of the complexes. Thus, acid complexes are not formed when the lanthanoid ion and the ligand form five-membered chelate rings, as in the oxalates<sup>5</sup> and oxydiacetates,<sup>6</sup> or when the coordinating groups are close to each other due to a rigid ligand geometry, as in the maleates.<sup>7</sup> The effectively bidentate ligands malonate and thiodiacetate form weaker chelate complexes,<sup>8,9</sup> and acid complexes are thus formed in appreciable amounts in these systems. The variation pattern of  $\text{p}K_a(\text{MHA}^{2+})$  versus the lanthanoid ion radius can be qualitatively described with simple electrostatic arguments.

This communication reports a determination of the composition and stability constants for scandium thiodiacetate complexes. The measurements have been designed to make it possible to decide if any scandium hydrogen thiodiacetate complex is formed. A potentiometric