

Molecular dynamics of sterically hindered dihalo- and diacyloxydiaryltelluranes

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Abstract

Dihalo- and diacyloxydi(2,6-dimethylphenyl)telluranes [10-Te-C₂X₂; X = halogen and RCO₂] were prepared and variable-temperature ¹H NMR studies revealed that these telluranes were composed of the sterically congested rotamers. The first examples of the activation parameters for rotation of the Te–C bonds were obtained in D NMR experiments.

Keywords: Tellurium; Chalcogen; Dynamics; Group 16; Hindered ligands; Nuclear magnetic resonances

1. Introduction

Organic hypervalent compounds of chalcogens have received considerable attention in the past two decades, and it has been predicted that the tellurium atom provides the most stable hypervalent compounds among the chalcogens [1–3]. However, there are no reports on the kinetic studies and the activation parameters for rotation of the Te–C bonds belonging to the tetracoordinated tellurium atom. In order to prevent the rotation of the equatorial Te–C bonds, we prepared sterically hindered telluranes having two electronegative halogens (**1**) [4] or acyloxy groups (**2**). In the course of the measurement of the ¹H NMR spectra of these compounds, we found that the two methyl groups attached at the 2,6-positions in the phenyl rings show different chemical shifts at room temperature and coalesce to a singlet at higher temperatures. This result indicates that the free rotation of the Te–C bonds in the tellurane **1a** would be prevented at room temperature. This paper describes the preparation of the sterically congested telluranes and the energy barriers for their rotations of the Te–C bonds by variable-temperature NMR studies.

2. Experimental and results

The telluranes **1a–d** and **2a–g** were prepared according to two routes, (A) [5] and (B) [6], as shown in Scheme 1. Their structures were confirmed by ¹H, ¹³C and ¹²⁵Te NMR spectroscopy and elemental analysis. The results together with ¹²⁵Te NMR data are summarized in Table 1.

The configuration of tellurane **1a** was finally determined by X-ray crystallographic analysis [7] and the ORTEP drawing (Fig. 1) demonstrates that the configuration around the tellurium atom in **1a** is a slightly distorted trigonal bipyramidal structure with two apical Te–Br bonds and two equatorial Te–C bonds which are closely located to interact with each other in the crystalline state [8]. The bond distances and angles of tellurane **1a** are shown in Fig. 1. It must be noted that the equatorial C–Te–C angle of **1a** is about 20° larger than that in dibromodiphenyltellurane (∠C–Te–C = 94.4°) [9]. The two bulky *o*-methyls interact sterically to expand the bond angles, thus it is predictable that the free rotation of the Te–C bonds are prevented.

Interestingly, examination of the ¹H NMR (270 MHz) spectrum of **1a** in CDCl₃ at room temperature showed the methyl protons as two broad singlets observed at 2.61 and 2.94 ppm. This spectrum may have two interpretations: (1) there are hindered rotations of the two aromatic rings along the axes of the equatorial carbon–

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Table 1
Yields, melting points, ^{125}Te NMR data and analytical data for telluranes

Compound	Yield (%)	M.p. (°C)	^{125}Te NMR (ppm) ^a	Found (%)		Calcd. (%)	
				C	H	C	H
1a	93	130	720	38.84	3.65	38.61	3.65
1b	58	210	784	46.55	4.37	47.01	4.44
1c ^b	88	227	1184 ^c	51.16	4.80	51.12	4.83
1d	93	201	721	40.08	3.90	39.90	3.94
2a	93	202	941	52.41	5.14	52.68	5.30
2b	98	258	1054	42.72	3.20	42.60	3.22
2c	100	203	945	53.29	5.54	53.66	5.58
2d	93	248	1060	43.59	3.45	43.64	3.49
2e	94	207	940	55.27	6.06	55.46	6.07
2f	86	199	919	58.42	6.94	58.52	6.91
2g	83	250	1013 ^d	48.13	4.20	48.14	4.44

^a Chemical shifts measured downfield from Me_2Te at room temperature.

^b **1c** was prepared by treatment of **1a** with 5 equiv. of KF.

^c $J(\text{Te}-\text{F}) = 769$ Hz.

^d At -5°C , the ^{125}Te NMR spectrum was found to split into the two peaks at 1011.0 and 1011.4 ppm in a 1:1 ratio arising from the diastereomer.

tellurium bonds: or (2) there are two stable conformers which arise by the pseudo-rotation of **1a**. However, since in general, halogen ligands are known to occupy the apical positions in hypervalent compounds [1], the formation of pseudo-rotamers can hardly be assumed. Furthermore, since the ^{125}Te NMR spectrum of **1a** in CDCl_3 from room temperature to -50°C showed only one peak at 720 ppm, the formation of pseudo-rotamers can rationally be excluded. We therefore concluded that the free rotation of the Te–C bonds is sterically retarded by the presence of the apical bromines and methyl groups at *ortho* positions. Furthermore, the ^1H NMR spectrum of **1a** shows that both the methyl and aromatic proton signals vary with temperature, i.e. the two methyl signals observed at 20°C coalesce to a singlet at 44.8°C (T_c) which is separated into the two singlets again on lowering the temperature, as shown in Fig. 2.

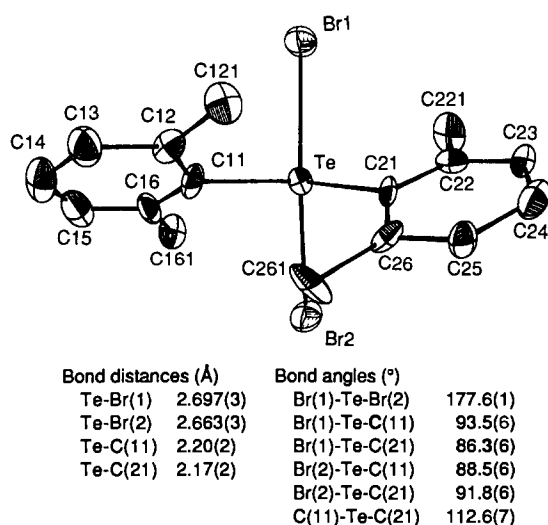
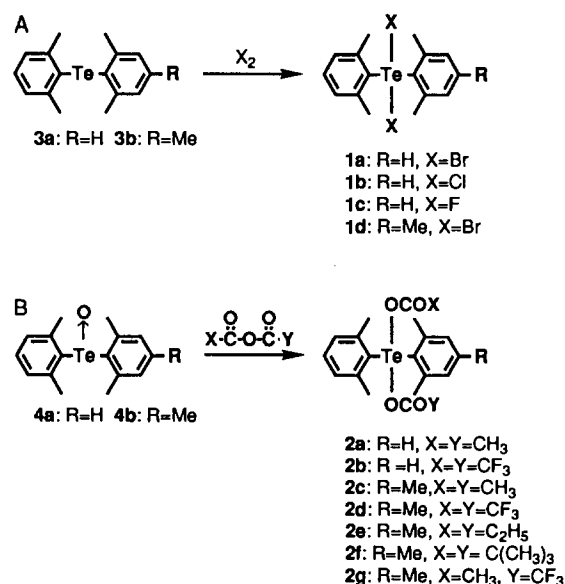


Fig. 1. ORTEP drawing of **1a**.

Using this T_c and the Shanan-Atidi equation, $\Delta G^\ddagger = 4.57(273 + T_c) \{9.97 + \log[(273 + T_c)/\Delta\text{Hz}]\}$ [10], the energy barrier for the free rotation of the equatorial carbon–tellurium bond in **1a** was calculated to be 15.2 kcal mol $^{-1}$ at 44.8°C in CDCl_3 . The ^1H NMR spectra of other halotelluranes **1b–d** and acyloxytelluranes **2a–g** were measured similarly and the results are presented in Table 2.

On the other hand, peak separation in the ^1H NMR spectra of both telluride **3** and telluroxide **4** was not observed with variable-temperature measurements indicating that the free rotation of Te–C bonds in telluranes **1** and **2** is restricted by the hypervalent structure which locks the conformational change.



Scheme 1.

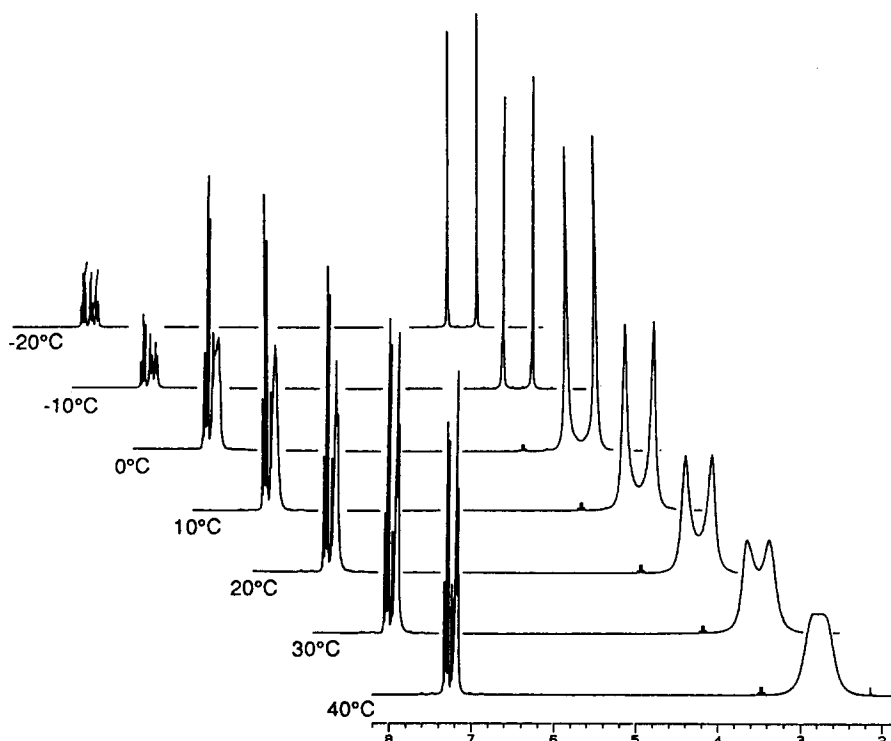


Fig. 2. Variable-temperature ^1H NMR spectra of **1a**.

Furthermore, the activation parameters of the rotation were evaluated from the simulation of the experimental spectra by analysing the simple two-site exchange model using tellurane **1a**. The rate constant k was obtained for each temperature by comparing the experimental spectra with simulated spectra as shown in Fig. 3 [11]. The plot of $\log(k/T)$ against $1/T$ gave a good straight line and the activation enthalpy (ΔH^\ddagger) and the activation entropy (ΔS^\ddagger) were calculated to be $10.82 \text{ kcal mol}^{-1}$ and $-13.54 \text{ cal mol}^{-1} \text{ K}^{-1}$, respectively, by a least-squares treatment using the Eyring model (see Fig. 4). These results indicate that the activation energy (ΔG^\ddagger) of **1a** is almost governed by the activation enthalpy (ΔH^\ddagger) and

the activation entropy (ΔS^\ddagger) is negative. The present studies on the variable-temperature NMR experiments provided the first example of the activation parameters of rotation of the equatorial Te–C bonds belonging to

Table 2
Free energy values

Compound	ΔG^\ddagger (kcal mol^{-1})	T_c ($^\circ\text{C}$)	Concentration (mmol^{-1})	Solvent
1a	15.2	44.8	37.2	CDCl_3
1b	17.9	60.0	44.4	CDCl_3
1c	16.9	79.8	47.0	CDCl_3
1d	18.1	70.0	36.3	CDCl_3
2a	21.2	149.5	40.3	Toluene- d_8
2b	22.1	150.0	33.6	Toluene- d_8
2c	23.8	155.0	39.2	Toluene- d_8
2d	22.4	144.5	32.4	Toluene- d_8
2e	22.8	160.0	38.2	Toluene- d_8
2f	23.0	155.0	36.2	Toluene- d_8
2g	18.9	95.0	35.5	Toluene- d_8

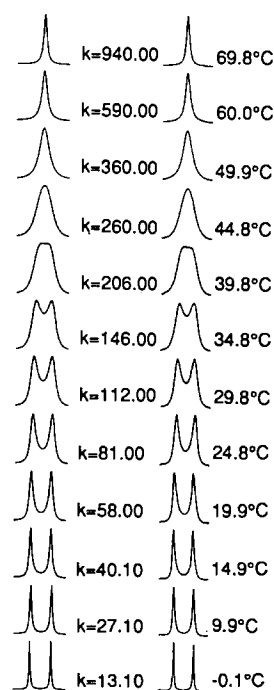


Fig. 3. Lineshape analysis of ^1H NMR spectra for **1a**. Left, calculated spectra; right, experimental spectra.

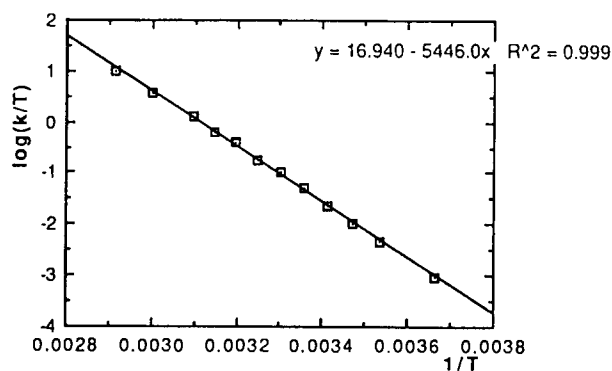


Fig. 4. Arrhenius plot for **1a**.

sterically hindered telluranes. It is interesting to note that **2g** is the first tetrasubstituted chiral tellurane. Further work is in progress to explore applications and advantages of sterically congested telluranes.

2.1. Supplementary material

Tables listing atomic coordinates, thermal parameters, bond distances, bond angles and anisotropic thermal parameters for non-hydrogen atoms have been deposited with the Cambridge Crystallographic Data Centre.

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References and notes

- [1] R.A. Hayes and J.C. Martin, *Sulfurane Chemistry*, in F. Bernardi, I.G. Csizmadia and A. Mangini (eds.), *Organic Sulfur Chemistry, Theoretical and Experimental Advances*, Elsevier, Amsterdam, 1985.
- [2] J.I. Musher, *Angew. Chem., Int. Ed. Engl.*, **8** (1969) 54; M.M.L. Chen and R. Hoffmann, *J. Am. Chem. Soc.*, **98** (1976) 1647; A.E. Reed and P. von R. Schleyer, *J. Am. Chem. Soc.*, **112** (1990) 1434; W. Kutzelnigg, *Angew. Chem., Int. Ed. Engl.*, **23** (1984) 272; A. Demolliens, O. Eisenstein, P.C. Hiberty, J.M. Lefour, G. Ohanessian, S.S. Shaik and F. Volatron, *J. Am. Chem. Soc.*, **111** (1989) 5623.
- [3] D.H.R. Barton, S.A. Glover, and S.V. Ley, *J. Chem. Soc. Chem. Commun.*, (1977) 266; D. Hellwinkel and G. Fahrback, *Liebigs Ann. Chem.*, **712** (1968) 1; I. Harigittai and B. Rozsondai, in S. Patai and Z. Rappoport (eds.), *The Chemistry of Organic Selenium and Tellurium Compounds*, Vol. 1, Wiley, Chichester, 1986, Chapt. 3, p. 63; J. Bergman, L. Engman, and J. Sidin, in S. Patai and Z. Rappoport (eds.), *The Chemistry of Organic Selenium and Tellurium Compounds*, Vol. 1, Wiley, Chichester, 1986, Chapt. 14, p. 517; D.B. Denney, D.Z. Denney, P.J. Hammond and Y.F. Hsu, *J. Am. Chem. Soc.*, **103** (1981) 2340; S. Ogawa, S. Sato, T. Erata and N. Furukawa, *Tetrahedron Lett.*, **33** (1992) 1915.
- [4] K. Lederer, *Chem. Ber.*, **49** (1916) 345.
- [5] F. Krafft and R.E. Lyons, *Chem. Ber.*, **27** (1984) 1768.
- [6] S. Tamagaki, I. Hatanaka and S. Kozuka, *Bull. Chem. Soc. Jpn.*, **50** (1977) 2501.
- [7] Crystallographic for Data **1a**: $F_w = 497.74$, orthorhombic, space group $P_{21}P_{21}P_{21}$, $a = 9.063(1)$, $b = 12.576(1)$, $c = 14.514(1)$ Å, $V = 1654(4)$ Å³, $Z = 4$, $R = 0.049$, $R_w = 0.066$ for 1697 reflections.
- [8] E.L. Mutterties and R.A. Schunn, *Q. Rev. Chem. Soc.*, **20** (1966) 245.
- [9] G.D. Christofferson and J.D. McCullough, *Acta Crystallogr.*, **11** (1958) 249.
- [10] H. Shanan-Atidi and K.H. Bar-Eli, *J. Phys. Chem.*, **74** (1970) 961.
- [11] H. Kihara and K. Mukai, *JAPC*, **7**, No. 2 (1985) 50.