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Synthesis and structure of novel heterocyclic aminotelluranes

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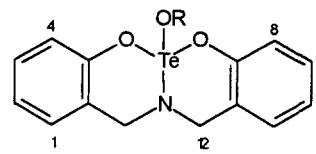
Abstract—A series of novel 6-alkoxy-12H,14H-[1,2,3]benzoxatellurazino[2,3-b]-[1,2,3]benzoxatellurazines **3** was synthesized from tetraalkoxytelluranes and bis(2-hydroxybenzyl)amines. ^{1}H, ^{13}C and ^{125}Te NMR studies suggest that these aminotelluranes, unlike their orthoamidoester analogs, have a rigid *trans*-fused conformation. A preferential *trans*-fused conformation was also deduced from *ab initio* MO calculations of a model oxatellurazinooxatellurazine **7**, using the STO-3G and SBK basis sets, and the Gaussian-92 program, which imply that the *trans*-fused aminotellurane is more stable than the corresponding *cis* isomer by 10.3 kcal/mol. © 1997 Elsevier Science Ltd

Keywords: Tetravalent tellurium; Oxatellurazines; ^{125}TeNMR; *ab initio* calculations; Tridentate ligands; Mannich bases.

Telluraheterocyclic ester derivatives of telluranic acid, $Te(OH)_4$ [1], have recently become of considerable interest due to their *in vitro* and *in vivo* immunomodulatory activity, such as ammonium-trichloro(dioxyethylene-O,O′)tellurate (AS-101) [2]. More recently, attention has been focused on the intriguing ligand exchange processes which take place in bidentate spirotelluranes, owing to their general trigonal bipyramidal structure [3,4].

While telluranes have been extensively studied, the synthesis and chemistry of the related acyclic and particularly cyclic aminotelluranes remain largely unexplored [5,6]. Our continuous interest in the structural dynamics and reactivity of telluranes led us to extend our studies toward novel telluranes and aminotelluranes containing tridentate ligands, in order further to verify the energy preferences of the various conformational isomers.

This work reports the synthesis and characterization of the first series of tridentate monoamidotelluranes of the type TeX_3YE (X = oxygen ligand, Y = nitrogen ligand, E = lone pair electrons), which have the novel heterocyclic structure of 6-alkoxy-12H,14H-[1,2,3]benzoxatellurazino[2,3-b][1,2,3]benzoxatellurazine **1**.



1 R = Alkyl

RESULTS AND DISCUSSION

Synthesis

A series of disubstituted [1,2,3]benzoxatellurazino[2,3-b][1,2,3]benzoxatellurazines **3** was prepared by reaction of tetraalkoxytelluranes $Te(OR)_4$ (R = Et, *i*-Pr) and bis(2-hydroxybenzyl)amines **2** [7] at room temperature, using the corresponding alcohols (ethanol or isopropanol) as the reaction solvents. All the compounds are thermodynamically stable in solution when kept under dry nitrogen, but quickly hydrolyze to the starting aminediols and TeO_2 when exposed to moist air.

† Part of the Ph.D. Thesis of I. Elyashiv, Bar-Ilan University, Ramat-Gan.

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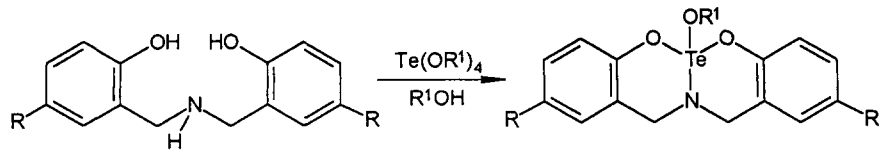

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R = H, Me, OMe, Cl, Br
R^1 = Et, i-Pr

3 a. R = H, R^1 = Et
b. R = Me, R^1 = Et
c. R = OMe, R^1 = Et
d. R = Cl, R^1 = Et
e. R = Br, R^1 = Et
f. R = H, R^1 = i-Pr
g. R = Me, R^1 = i-Pr
h. R = OMe, R^1 = i-Pr
i. R = Cl, R^1 = i-Pr
j. R = Br, R^1 = i-Pr

NMR analysis

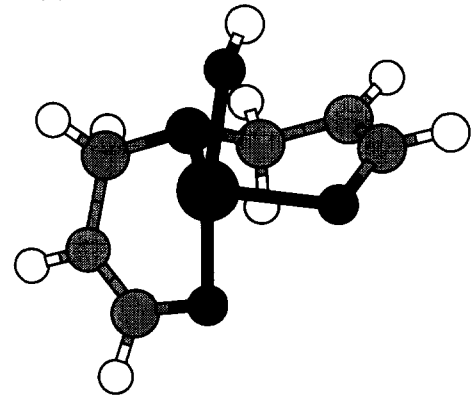
The ^1H NMR spectra of **3** in DMSO-d_6 or CD_3CN all show a characteristic AB quartet of the cyclic methylene protons at δ 4.1–5.1 ppm region, whereas the $^{13}C\{^1H\}$ NMR spectra exhibit a single peak of the corresponding carbon at δ 53.4–56.0 ppm. The characteristic wide signals of ^{125}Te all appear within a narrow range δ 1394–1418 ($\nu_{1/2}$ = 30–75 Hz).

The proton spectra remain essentially unchanged upon lowering the temperature [8], suggesting that in the *trigonal bipyramidal* (TBP) bicyclic aminotelluranes **3** the *O,O*-axial-*N*-equatorial (*trans*-fused) geometry (Fig. 1b) of the oxatellurazino rings is preferred over the *O*-axial-*N,O*-equatorial (*cis*-fused) geometry (Fig. 1a), and with a relatively high (>15 kcal/mol) barrier of *cis–trans* interconversion. Notably, [1,3]benzoxazino[2,3-b][1,3]benzoxazines **4**, the *tetrahedral* orthoaminoester carbon-analogs of **3**, exhibit temperature dependent NMR spectra [9].

Mass spectra

Aminotelluranes **3** exhibit a common fragmentation pattern in the mass spectrum, which obeys the 'even-electron rule' [10] and is summarized in Scheme 1. A major fragmentation pathway involves the initial loss of an RO· radical from the parent radical cation to give the corresponding $[M\text{-}RO]^+$ cation, which undergoes a retro-Diels–Alder reaction yielding the benzoxatellurazine $[RC_7H_5NOTe]^+$ cation (and a neutral *ortho*quinone methide fragment RC_7H_5O). This fragmentation pathway was confirmed by B/E, B/E^2 and neutral loss linked scan MS/MS measurements. Interestingly, the analogous benzoxazinobenzoxazines undergo an efficient thermal cycloreversion to *ortho*quinone methide **5** and 1,3-benzoxazine **6** [9]. Alternatively, the parent radical cation loses an alcohol (R^1OH) and CO molecules to give $[R_2C_{13}H_9NOTe]^{\cdot+}$ radical cation, which subsequently cleaves by loss of a neutral RC_6H_5 fragment to benzoxatellurazine $[RC_7H_4NOTe]^{\cdot+}$ radical cation.

(a) *Cis*-7



(b) *Trans*-7

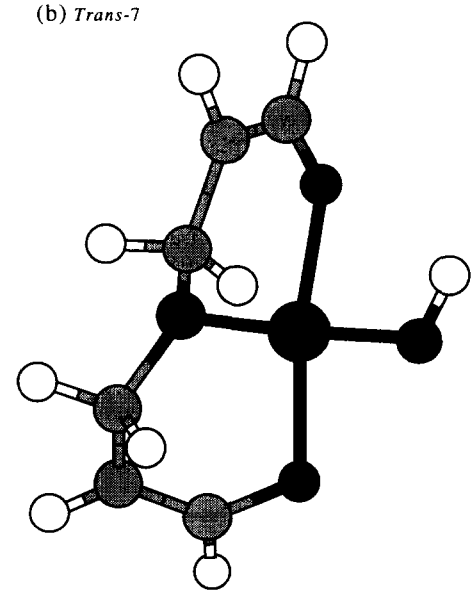
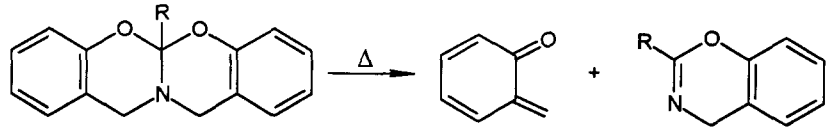


Fig. 1. Calculated structures of (a) *cis*-7 and (b) *trans*-7 aminotelluranes.



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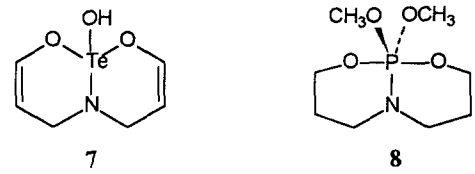
Structural analysis by ab initio *MO calculations*

There remains the question of the geometry around the tellurium atom. X-ray structural analysis of spiro telluranes [11] show the tellurium atom to be surrounded by four oxygen atoms providing a distorted trigonal bipyramidal environment of the type AX_4E (where A is Te, X is a ligand, and E is the electron lone pair on the tellurium atom), with one equatorial position vacant. In general, ring systems preferably span the axial-equatorial positions (minimum ring-strain), with the more electronegative groups occupying the axial positions (polarity rule) [12,13]. Hence, when two heteroatoms are present, e.g. oxygen and nitrogen, as in the bicyclic telluranes **3**, it is expected that the nitrogen and the nonring alkoxy groups will preferentially occupy the equatorial position.

We have carried out *ab initio* MO calculations of the bicyclic oxatellurazinooxatellurazine system **7** as a model structure of **3**, using the STO-3G and the SBK basis sets [14] and the Gaussian-92 program [15]. Preliminary calculations of a series of tetravalent tellurium compounds with known X-ray structural analysis, e.g. TeF_4 [16], TeI_2Me_2 [17], $TeCl_2Me_2$ [18], and $TeCl_2Et_2$ [19], have shown a good fit between the



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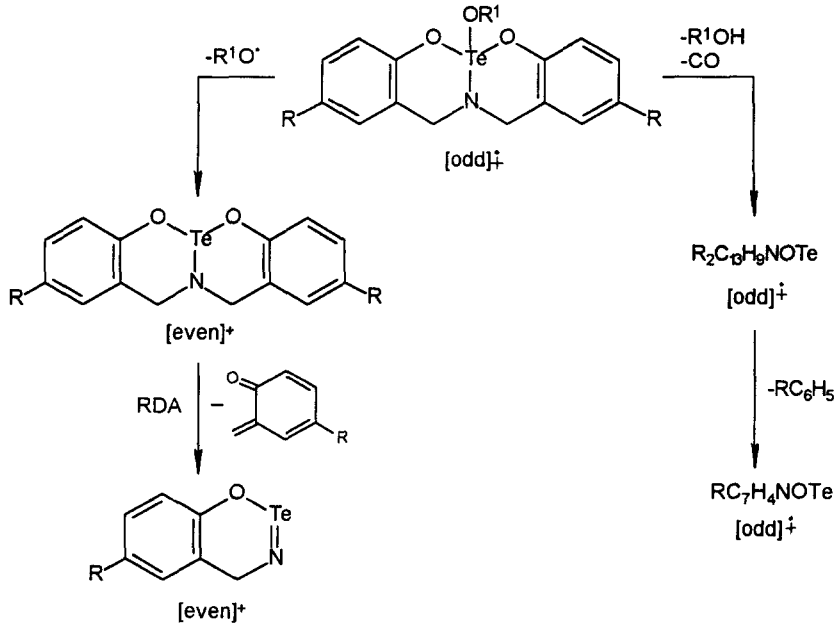
experimental and SBK basis set results. Similarly, a good correlation between the *ab initio* calculations of the spirotellurane $Te(O_2C_2H_4)_2$ and the X-ray structural data of spiropinacol derivative $Te(O_2C_6H_{12})_2$ [11] was noticed.

The calculated geometrical parameters of the two basic structures of the bicyclic model: the *cis*-fused (Fig. 1a) and *trans*-fused (Fig. 1b) isomers of **7**, are listed in Table 1 [20]. In both isomers, the nitrogen atom occupies the equatorial position. The *trans* isomer was found to be more stable by 10.3 kcal/mol than the *cis* isomer.

It is interesting to note that the analogous cyclic TBP phosphorane **8** [21] also exhibits a geometry in which the nitrogen and the two noncyclic methoxy substituents occupy equatorial positions. Thus, in bicyclic TBP phosphoranes and telluranes, the *trans*-fused configuration, where the six-membered rings



Scheme 1. Fragmentation pattern of aminotelluranes **3** in the mass spectrum.

Table 1. Calculated geometrical parameters for the *cis*- and *trans*-fused aminotelluranes 7[a]

		Cis-7		*Trans*-7	
		STO-3G	SBK	STO-3G	SBK
Relative Energy[b]		11.90	10.30	0.00	0.00
Axial axis					
	Te—O(1)	2.028	2.097	1.999	2.042
	Te—O(2)	1.975	1.961	1.996	2.030
	O(1)—Te—O(2)	148.9	170.0	139.5	166.0
Equatorial plane					
	Te—O(3)	1.980	1.915	1.978	1.907
	Te—N	2.034	1.997	2.018	1.972
	O(3)—Te—N	107.7	98.1	127.7	105.0
Other bond angles					
	O(1)—Te—O(3)	76.6	82.6	75.7	82.1
	O(1)—Te—N	82.2	85.1	86.3	90.7
	O(2)—Te—O(3)	82.2	90.0	80.4	84.7
	O(2)—Te—N	83.0	89.3	83.0	88.2

[a] Bond length in Å, bond angles in degrees (°).
[b] Relative energy in kcal/mol.

span the axial-equatorial geometry, is favorably adopted.

EXPERIMENTAL

Instrumentation

^{1}H, ^{13}C and ^{125}Te NMR spectra were recorded on a Bruker AM-300 spectrometer. ^{1}H and ^{13}C chemical shifts are referred to internal TMS standard. For ^{125}Te a spectrum of 0.42 M Ph_2Te in $CDCl_3$ was taken as standard and the tellurium line obtained was calibrated at 688 ppm (neat Me_2Te is 0 ppm) [22]. The alkoxy groups proton signals of compounds **3** are usually not reported, since they overlap with the signals of excess of the corresponding tetraalkoxytellurans. Mass spectra were recorded on a Finnigan 4020 Quadrupole LR and a Fisions VG Auto Spec. HR instrument. Direct insertion probe in the EI mode was carried out in all MS measurements. The following settings of the magnetic instrument were used to achieve a maximum signal: source temperature 180°C, electron energy 70 eV, acceleration voltage 8000 V. The magnetic sector of the instrument was operated at a resolution of 10,000 for exact mass determination and at a resolution of 1000 for B/E, B^2/E linked scan measurements. The molecular weights were calculated for the following isotopes: ^{130}Te, ^{35}Cl, ^{79}Br.

Materials

All alcohols and solvents were dried prior to use. A freshly opened bottle of $TeCl_4$ (Merck) was used without any treatment.

Tetraethoxytellurane and tetraisopropoxytellurane were prepared by methods described elsewhere [3], Bis(2-hydroxylbenzyl)amines **2** were prepared by modification of known procedures [7].

General procedure for the preparation of 6-*alkoxy*-12*H*,14*H*-[1,2,3]*benzoxatellurazino*[2,3-*b*][1,2,3]*benzoxatellurazines* **3**

Tetraethoxy or tetraisopropoxytellurane (4.8 mmol) was added with stirring to a solution of **2** (3 mmol) in 0.5 cm^3 of ethanol or isopropanol, respectively. The mixture was stirred at room temperature for 3 h. The alcohol and the excess of tetraethoxy or tetraisopropoxytellurane was removed by distillation *in vacuo* (5×10^{-3} torr), leaving **3** as a light yellow–orange viscous oil (95–98% yield), containing <2% (by NMR) of the starting tetraalkoxytellurane, which was difficult to remove. Compounds **3** were sensitive to light and moisture and were stored in the dark at 5°C.

6-*Ethoxy*-12*H*,14*H*-[1,2,3]*benzoxatellurazino*[2,3-*b*][1,2,3]*benzoxatellurazine* **3a**

^{1}H NMR (DMSO-d_6): δ 4.20 (d, J = 12.5 Hz, 2H), 4.97 (d, J = 12.5 Hz, 2H), 6.63 (td, J = 8, 1.5 Hz, 2H), 6.77 (dd, J = 8, 1.5 Hz, 2H), 7.07 (td, J = 8, 1.5 Hz, 2H). ^{13}C NMR (DMSO-d_6): δ 18.05 (CH_3), 54.08 (CH_2), 57.44 (CH_2), 117.46 (CH), 117.82 (CH), 124.13 (C), 126.93 (CH), 127.75 (CH), 156.54 (C). ^{125}Te NMR (0.39 M, DMSO-d_6) 1418 ppm ($\nu_{1/2}$ = 30 Hz). EIMS *m/e* (%): 356 (0.27, M-OCH_2CH_3), 355 (0.18, M-CH_3CH_2OH), 327 (0.02, M-CH_3CH_2OH-CO), 294 (0.18, M-C_7H_7O), 250 (0.6, M-CH_3CH_2O-C_7H_8O), 249 (1.1, M-CH_3CH_2OH-C_7H_8O), 121 (0.23, C_7H_7NO), 120 (2.17, C_7H_6NO), 107 (1.09, C_7H_7O),

78 (2.06, C_6H_6). HRMS for $C_{16}H_{17}O_3NTe$ Calcd: 401.027, Found: 401.019.

2,10-*Dimethyl*-6-*ethoxy*-12*H*,14*H*-[1,2,3]*benzoxatellurazino*[2,3-*b*][1,2,3]*benzoxatellurazine* **3b**

^{1}H NMR (DMSO-d_6): δ 2.18 (s, 6H), 4.09 (d, J = 11.5 Hz, 2H), 4.94 (d, J = 11.5 Hz, 2H), 6.50 (d, J = 8 Hz, 2H), 6.83 (bs, 2H), 6.89 (d, J = 8 Hz, 2H). ^{13}C NMR (DMSO-d_6): δ 18.99 (CH_3), 21.10 (CH_3), 58.55 (CH_2), 54.61 (CH_2), 117.64 (CH), 127.91 (CH), 127.99 (*C*-CH_3), 128.57 (CH), 126.66 (C), 154.50 (C). ^{125}Te NMR (0.41 M, DMSO-d_6) 1403 ppm ($\nu_{1/2}$ = 35 Hz). EIMS *m/e* (%): 384 (0.15, M-OCH_2CH_3), 383 (0.03, M—CH_3CH_2OH), 355 (0.06, M-CH_3CH_2OH-CO), 308 (0.31, M—$C_8H_9O^-$), 264 (5.5, M-CH_3CH_2O-$C_8H_{10}O$), 263 (11, M-CH_3CH_2OH-$C_8H_{10}O$), 135 (1.25, M-C_8H_9NO), 134 (4.86, C_8H_8NO), 121 (3.36, C_8H_9O), 92 (0.95, C_7H_8). HRMS for $C_{18}H_{21}O_3NTe$ Calcd: 429.058, Found: 429.050.

2,10-*Dimethoxy*-6-*ethoxy*-12*H*,14*H*-[1,2,3]*benzoxatellurazino*[2,3-*b*][1,2,3]*benzoxatellurazine* **3c**

^{1}H NMR (DMSO-d_6): δ 3.65 (s, 6H), 4.18 (d, J = 11.5 Hz, 2H), 4.91 (d, J = 11.5 Hz, 2H), 6.54 (d, J = 8 Hz, 2H), 6.65 (bs, 2H), 6.70 (d, J = 8 Hz, 2H). ^{13}C NMR (DMSO-d_6): δ 18.49 (CH_3), 55.27 (OCH_3), 55.54 (CH_2), 56.87 (CH_2), 112.88 (CH), 113.54 (CH), 118.26 (CH), 128.68 (C), 150.47 (C), 151.78 (*C*-OCH_3). ^{125}Te NMR (0.38 M, DMSO-d_6): 1399 ppm ($\nu_{1/2}$ = 75 Hz). EIMS *m/e* (%): 416 (5.72, M-OCH_2CH_3), 415 (2.83, M-CH_3CH_2OH), 387 (1.14, M-CH_3CH_2OH-CO), 324 (1.73, M-$C_8H_9O_2$), 280 (6.15, M-CH_3CH_2-$C_8H_{10}O_2$), 279 (8.63, M-CH_3CH_2OH-$C_8H_{10}O_2$), 151 (10.02, $C_8H_9NO_2$), 150 (17.69, $C_8H_8NO_2$), 137 (16.63, $C_8H_9O_2$), 108 (14.78, C_7H_8O). HRMS for $C_{18}H_{21}O_5NTe$ Calcd: 461.048, Found: 461.042.

2,10-*Dichloro*-6-*ethoxy*-12*H*,14*H*-[1,2,3]*benzoxatellurazino*[2,3-*b*][1,2,3]*benzoxatellurazine* **3d**

^{1}H NMR (DMSO-d_6): δ 4.21 (d, J = 11.5 Hz, 2H), 4.84 (d, J = 11.5 Hz, 2H), 6.63 (d, J = 8 Hz, 2H), 7.10 (bs, 2H), 7.15 (bs, 2H). ^{13}C NMR (DMSO-d_6): δ 18.45 (CH_3), 53.42 (CH_2), 55.95 (CH_2), 119.63 (CH), 121.70 (C-Cl), 127.08 (CH), 127.90 (CH), 130.04 (C), 155.73 (C). ^{125}Te NMR (0.37 M, DMSO-d_6): 1394 ppm ($\nu_{1/2}$ = 60 Hz). EIMS *m/e* (%): 424 (4.57, $MOCH_2CH_3$), 423 (7.99, M-CH_3CH_2OH), 395 (0.02, M-CH_3CH_2OH-CO), 328 (0.36, M-ClC_7H_6O), 284 (0.80, M-CH_3CH_2O-ClC_7H_7O), 283 (1.69, M-CH_3CH_2OH-ClC_7H_7O), 155 (1.63, ClC_7H_6NO), 154 (5.45, ClC_7H_5NO), 141 (4.87, ClC_7H_6O), 112 (1.89, ClC_6H_5). HRMS for $C_{16}H_{15}Cl_2O_3NTe$ Calcd: 468.949, Found: 468.956.

2,10-*Dibromo*-6-*ethoxy*-12*H*,14*H*-[1,2,3]*benzoxatellurazino*[2,3-*b*][1,2,3]*benzoxatellurazine* **3e**

^{1}H NMR (DMSO-d_6): δ 4.16 (d, J = 12 Hz, 2H), 4.83 (d, J = 12 Hz, 2H), 6.60 (d, J = 8 Hz, 2H), 7.20 (bs, 2H), 7.23 (bs, 2H). ^{13}C NMR (DMSO-d_6): δ 18.64 (CH_3), 53.39 (CH_2), 57.96 (CH_2), 109.42 (C-Br), 120.20 (CH), 129.86 (CH), 130.71 (C), 130.77 (CH), 156.26 (C). ^{125}Te NMR (0.40 M, DMSO-d_6): 1395 ppm ($\nu_{1/2}$ = 60 Hz). EIMS *m/e* (%): 512 (5.53, M-OCH_2CH_3), 511 (9.05, M-CH_3CH_2OH), 483 (9.33, M-CH_3CH_2OH-CO), 372 (4.10, M-BrC_7H_6O), 328 (0.14, M-CH_3CH_2O-BrC_7H_7O), 327 (0.35, M-CH_3CH_2OH-BrC_7H_7O), 199 (52.07, BrC_7H_6NO), 198 (20.45, BrC_7H_5NO), 185 (4.92, BrC_7H_6O), 156 (6.64, BrC_6H_5). HRMS for $C_{16}H_{15}Br_2O_3NTe$ Calcd: 556.848, Found: 556.856.

6-(2-*Propoxy*)-12*H*,14*H*-[1,2,3]*benzoxatellurazino*[2,3-*b*][1,2,3]*benzoxatellurazine* **3f**

^{1}H NMR (CD_3CN): δ 4.07 (d, J = 11.5 Hz, 2H), 5.03 (d, J = 11.5 Hz, 2H), 6.69 (dd, J = 8, 1.5 Hz, 2H), 6.79 (td, J = 8, 1.5 Hz, 2H), 7.07 (dd, J = 8, 1.5 Hz, 2H), 7.16 (td, J = 8, 1.5 Hz, 2H). ^{13}C NMR (CD_3CN): δ 26.34 (CH_3), 55.95 (CH_2), 66.08 (CH), 119.65 (CH), 120.42 (CH), 128.46 (CH), 129.55 (C), 129.67 (CH), 157.33 (C). ^{125}Te NMR (0.42 M, DMSO-d_6): 1418 ppm ($\nu_{1/2}$ = 30 Hz). EIMS *m/e* (%): 356 (12.53, M-$OCH(CH_3)_2$), 355 (9.82, M-$(CH_3)_2CHOH$), 327 (1.7, M-$(CH_3)_2CHOH$-CO), 308 (0.77, M-C_7H_7O), 250 (11.14, M-$(CH_3)_2CHO$ C_7H_8O), 249 (21.0, M-$(CH_3)_2CHOH$-C_7H_8O), 121 (35.94, [C_7H_7NO]), 120 (35.67, C_7H_6NO), 107 (33.19, C_7H_7O), 78 (23.15, C_6H_6). HRMS for $C_{17}H_{19}O_3NTe$ Calcd: 415.042, Found: 415.035.

2,10-*Dimethyl*-6-(2-*propoxy*)-12*H*,14*H*-[1,2,3]-*benzoxatellurazino*[2,3-*b*][1,2,3]-*benzoxatellurazine* **3g**

^{1}H NMR (DMSO-d_6): δ 2.20 (s, 6H), 4.10 (d, J = 12 Hz, 2H), 5.03 (d, J = 12 Hz, 2H), 6.49 (d, J = 7.5 Hz, 2H), 6.83 (bs, 2H), 6.93 (dd, J = 8, 2 Hz, 2H). ^{13}C NMR (DMSO-d_6): 21.10 (CH_3), 25.13 (CH_3), 54.90 (CH_2), 66.12 (CH), 117.66 (CH), 126.53 (C), 127.93 (CH), 127.93 (*C*-CH_3), 128.44 (CH), 154.39 (C). ^{125}Te NMR (0.38 M, DMSO-d_6): 1418 ppm ($\nu_{1/2}$ = 30 Hz). EIMS *m/e* (%): 384 (3.7, M-$OCH(CH_3)_2$, 3.83 (0.45, M-$(CH_3)_2CHOH$), 355 (35.45, M-$(CH_3)_2CHOH$-CO), 322 (0.97, M-C_8H_9O), 264 (3.35, M-$(CH_3)_2CHO$-$C_8H_{10}O$), 263 (15.2, M-$(CH_3)_2CHOH$-$C_8H_{10}O$), 135 (1.30, C_8H_9NO), 134 (13.9, C_8H_8NO), 121 (9.78, C_8H_8NO), 92 (3.1, C_7H_8). HRMS for $C_{19}H_{23}O_3NTe$ Calcd: 443.074, Found: 443.061.

2,10-*Dimethoxy*-6-(2-*propoxy*)-12*H*,14*H*-[1,2,3]*benzoxatellurazino*[2,3-*b*][1,2,3]-*benzoxatellurazine* **3h**

^{1}H NMR (CD_3CN): δ 3.68 (s, 6H), 4.23 (d, J = 12 Hz, 2H), 4.96 (d, J = 1 Hz, 2H), 6.61 (d, J = 8 Hz,

2H), 6.67 (d, $J = 7.5$ Hz, 2H), 6.73 (dd, $J = 8$, 2 Hz, 2H). ^{13}C NMR (CD_3CN): 26.21 (CH_3), 56.34 (OCH_3), 56.08 (CH_2), 66.0 (CH), 113.90 (CH), 114.89 (CH), 120.07 (CH), 130.06 (C), 150.99 (C), 154.02 (*C*-OCH_3). ^{125}Te NMR (0.41 M, DMSO-d_6): 1413 ppm ($\nu_{1/2} = 60$ Hz). EIMS *m/e* (%): 4.16 (17.77, M-$OCH(CH_3)_2$), 415 (6.9, M-$(CH_3)_2CHOH$), 338 (1.30, M-$C_8H_9O_2$), 280 (11.02, M-$(CH_3)_2CHO$-$C_8H_{10}O_2$), 279 (16.75, M-$(CH_3)_2CHOH$-$C_8H_{10}O_2$), 151 (29.40, $C_8H_9NO_2$), 150 (36.1, $C_8H_8NO_2$), 137 (6.95, $C_8H_9O_2$), 108 (15.6, C_7H_8O). HRMS for $C_{19}H_{23}O_5NTe$ Calcd: 475.063, Found: 475.067.

2,10-*Dichloro*-6-(2-*propoxy*)-12*H*,14*H*-[1,2,3]*benzoxatellurazino*[2,3-*b*][1,2,3]-*benzoxatellurazine* **3i**

^{1}H NMR (DMSO-d_6): δ 4.18 (d, $J = 12$ Hz, 2H), 4.93 (d, $J = 12$ Hz, 2H), 6.62 (d, $J = 8$ Hz, 2H), 7.11 (bs, 2H), 7.14 (dd, $J = 8.2$ Hz, 2H). ^{13}C NMR (DMSO-d_6): 25.99 (CH_3), 53.79 (CH_2), 63.98 (CH), 119.66 (CH), 121.69 (C-Cl), 127.09 (CH), 127.83 (CH), 130.04 (C), 155.71 (C). ^{125}Te NMR (0.38 M, DMSO-d_6): 1410 ppm ($\nu_{1/2} = 40$ Hz). EIMS *m/e* (%): 424 (14.74, M-$OCH(CH_3)_2$), 423 (4.41, M-$(CH_3)_2CHOH$), 342 (1.24, M-ClC_7H_6O), 284 (3.29, M-$(CH_3)_2CHO$-ClC_7H_7O), 283 (9.13, M-$(CH_3)_2CHOH$-ClC_7H_7O), 155 (15.03, ClC_7H_6NO), 154 (15.00, ClC_7H_6O), 141 (13.97, ClC_7H_6O), 112 (4.39, ClC_6H_5). HRMS for $C_{17}H_{17}Cl_2O_3NTe$ Calcd: 482.964, Found: 482.969.

2,10-*Dibromo*-6-(2-*propoxy*)-12*H*,14*H*-[1,2,3]*benzoxatellurazino*[2,3-*b*][1,2,3]-*benzoxatellurazine* **3j**

^{1}H NMR (DMSO-d_6): 0.82 (d, $J = 6.6$ Hz, 6H), 4.20 (d, $J = 11.8$ Hz, 2H), 4.32 (sep., $J = 6.6$ Hz, 1H), 4.94 (d, $J = 11.8$ Hz, 2H), 6.58 (d, $J = 8$ Hz, 2H), 7.22 (bs, 2H), 7.27 (d, $J = 8$ Hz, 2H). ^{13}C NMR (DMSO-d_6): 26.07 (CH_3), 53.65 (CH_2), 65.06 (CH), 109.30 (C-Br), 120.23 (CH), 129.87 (CH), 130.66 (C), 130.70 (CH), 156.05 (C). ^{125}Te NMR (0.39 M, DMSO-d_6): 1411 ppm ($\nu_{1/2} = 50$ Hz). EIMS *m/e* (%): 512 (13.44, M-$OCH(CH_3)_2$), 511 (1.96, M-$(CH_3)_2CHOH$), 386 (2.32, M-BrC_7H_6O), 328 (5.53, M-$(CH_3)_2CHO$-BrC_7H_7O), 327 (12.67, M-$(CH_3)_2CHOH$-BrC_7H_7O), 199 (19.08, BrC_7H_6NO), 198 (17.42, BrC_7H_5NO), 185 (18.56, BrC_7H_6O), 156 (10.53, BrC_6H_5). HRMS for $C_{17}H_{17}Br_2O_3NTe$ Calcd: 570.861, Found: 570.856.

Supplementary data available— Calculated *vs* X-ray data of Te^{IV} compounds TeF_4, TeI_2Me_2, $TeCl_2Me_2$ and $TeCl_2Et_2$, are given in Table S1, and of spirotellurane $(C_2H_4O_2)_2Te$, in Table S2 (2 pages). Ordering information is given on any current masthead paper.

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20. The STO-3G, being a minimal basis-set, gives only an approximate description of the electron density distribution of the molecule. Nevertheless, it is the only 'standard', all electron basis set which includes 4th row elements such as tellurium. The SBK, an ECP basis-set, which is believed to give a better description of the valence electrons, does not treat the core electrons explicitly, but rather approximates them *via* an 'effective core potential'. Hence we felt the need to quote the results of each method. The STO-3G geometry, while probably cruder than that of the SBK, shows a similar bent structure (O(1)—Te—O(2) angle), and its conformational energy is very close. In any case the conclusions regarding the relative thermodynamic stabilities of the two isomers are the same.
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