

Molecular Structures of Dibromo [(*E*)-2-bromo-2-phenylvinyl]-(phenyl)tellurium(IV) and Dibromo [(*Z*)-2-bromo-2-phenylvinyl] (*p*-tolyl)tellurium(IV) hydrate methanolate

LU, Wei-Min^{*,a} (陆维敏) WANG, Ya-Pin^a (王亚萍) HUANG, Xian^a (黄宪) SUN, Jie^b (孙杰)

^a Chemistry Department, Zhejiang University (Xixi Campus), Hangzhou, Zhejiang 310028, China

^b Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Science, Shanghai 200032, China

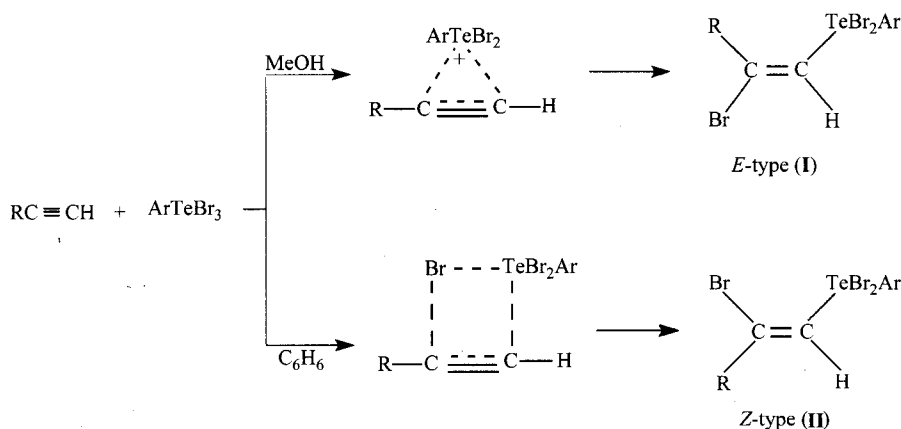
The structures of title compounds, [TeBr₂(C₈H₆Br)(C₆H₅)] (I) and [TeBr₂(C₈H₆Br)(C₇H₉)](H₂O)(CH₃OH) (II), have been determined by X-ray diffraction. The structures confirm that *E*- or *Z*-type configuration of vinylic telluride depends on the polarity of solvent employed. In either structure, Te atom is in a trigonal dipyramide configuration with the lone pair of electrons in the equatorial position.

Keywords Crystal structure, vinylic telluride

The applications of vinylic tellurides in organic syn-

thesis are considered as important intermediates, especially in the stereoselective formation of olefin derivatives.¹⁻³ The structures of the title compounds were determined, not only for postulation of the structures of the intermediates in their syntheses of trisubstituted alkenes, but also for confirmation of the *Z*- or *E*-type configurations affected by different solvents. Anti addition product (*E*-type) (I) was obtained almost exclusively in a polar solvent and *Z*-isomer by 93—98% in a nonpolar solvent.⁴

Scheme 1



* E-mail: weimwlu@mail.hz.zj.cn

Received October 17, 2000; revised December 18, 2000; accepted December 19, 2000.

Project supported by the National Natural Science Foundation of China.

Experimental

The crude products of the title compounds were prepared as the reported method.⁴ The crystals of **I** suitable for X-ray work were obtained by recrystallization from the mixed solvent of CHCl₃ and CH₃OH (10:1 ratio) and **II** from the mixed solvent of CH₃Cl and C₆H₆ (10:1 ratio).

Both structures were solved by direct methods and expanded using Fourier technique. The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included but not refined. All calculations were performed using the texsan crystallographic software package of Molecular Structure Corporation. Details are given in Table 1 and the complete data are available from the authors upon request.

Table 1 Crystal and data collection parameters for complexes **I** and **II**

	Crystal data for I	Crystal data for II
Molecular formula	C ₁₄ H ₁₁ Br ₃ Te	C ₁₆ H ₁₉ Br ₃ O ₂ Te
Molecular weight	546.55	610.64
Crystal system	Monoclinic	Orthorhombic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ 2 ₁ 2
<i>a</i> (nm)	0.9968(1)	1.8128(3)
<i>b</i> (nm)	0.8620(2)	0.8302(2)
<i>c</i> (nm)	1.8204(7)	1.2808(5)
β (°)	90.61(2)°	
<i>V</i> (nm ³)	1.5641(7)	1.927(1)
<i>Z</i>	4	4
<i>D</i> _x (g/cm ³)	2.32	2.104
λ (nm, Mo K _α)	0.071069	0.071069
μ (mm ⁻¹)	9.57	7.785
<i>T</i> (K)	293	293
Size (mm)	0.30 × 0.20 × 0.20	0.30 × 0.20 × 0.20
Color	Yellow	Yellow
Diffractometer	Rigaku AFC7R diffractometer	Rigaku AFC7R diffractometer
Scan	ω/2θ	ω/2θ
Absorption correction	ψ scans (Walke, DIFABS, 1983)	ψ scans (Walke, DIFABS, 1983)
<i>T</i> _{max}	1.132	1.059
<i>T</i> _{min}	0.904	0.874
Measured reflections	1900	1521
Independent reflections	1755	1491
Observed reflections [<i>I</i> > 3σ(<i>I</i>)]	1302	1253
Refinement	On <i>F</i>	On <i>F</i>
R _{int}	0.129	0.142
θ _{max} (°)	22.5	23.8
<i>h</i>	0–9	0–19
<i>k</i>	0–9	0–9
<i>l</i>	–19–19	0–13
Intensity decay (%)	–1.94	–1.49
<i>w</i>	1/σ ² (<i>F</i>)	1/σ ² (<i>F</i>)
(Δ/σ) _{max}	0.01	0.09
Δρ _{max} (e/nm ³)	0.00044	0.00097
Δρ _{min} (e/nm ³)	–0.00039	–0.00081
<i>R</i>	0.024	0.042
<i>wR</i>	0.039	0.054
<i>S</i>	1.20	1.82
Number of refined parameters	164	200
H atoms	Not refined	Not refined
Extinction (Zachariasen, 1963)	2.937 e-07	2.60854 e-07

Result and discussion

Final atomic coordinates and equivalent temperature

factors for non-hydrogen atoms are given in Table 2. Selected bond distances and angles are listed in Table 3. Fig. 1 shows an ORTEP diagram of the molecular structures with the numbering scheme.

Table 2 Fractional coordinates and equivalent isotropic temperature factors of the non-H atoms

Compound I				
Atom	x/a	y/b	z/c	U_{ij}
Te	0.22025(6)	0.05238(6)	0.20450(3)	0.0306(2)
Br(1)	-0.0118(1)	-0.0593(1)	0.24891(6)	0.0531(4)
Br(2)	0.46268(10)	0.1499(1)	0.15545(5)	0.0396(3)
Br(3)	0.33149(9)	-0.47594(10)	0.15104(5)	0.0362(3)
C(1)	0.2967(9)	-0.174(1)	0.2012(4)	0.031(3)
C(2)	0.2635(8)	-0.2681(10)	0.1464(4)	0.027(2)
C(3)	0.1854(8)	-0.233(1)	0.0794(5)	0.031(3)
C(4)	0.2338(9)	-0.127(1)	0.0286(5)	0.042(3)
C(5)	0.168(1)	-0.100(1)	-0.0364(6)	0.047(3)
C(6)	0.051(1)	-0.179(1)	-0.0520(5)	0.047(3)
C(7)	-0.0021(10)	-0.282(1)	-0.0010(6)	0.049(3)
C(8)	0.0654(10)	-0.309(1)	0.0626(6)	0.044(3)
C(9)	0.2832(8)	0.095(1)	0.3138(5)	0.028(3)
C(10)	0.2743(10)	-0.022(1)	0.3662(5)	0.036(3)
C(11)	0.3190(10)	0.009(1)	0.4375(5)	0.041(3)
C(12)	0.3700(9)	0.153(1)	0.4556(4)	0.038(3)
C(13)	0.3755(9)	0.268(1)	0.4023(5)	0.039(3)
C(14)	0.3338(8)	0.238(1)	0.3311(4)	0.032(3)
Compound II				
Atom	x/a	y/b	z/c	U_{ij}
Te	0.21688(6)	0.0337(1)	0.61191(8)	0.0463(3)
Br(1)	0.3247(1)	0.0060(2)	0.8240(1)	0.0627(6)
Br(2)	0.32748(9)	-0.0708(2)	0.4861(2)	0.0613(6)
Br(3)	0.1117(1)	0.1138(3)	0.7437(2)	0.0790(7)
O(1)	0.458(1)	0.170(3)	0.124(2)	0.16(1)
O(2)	0.9733(7)	0.474(3)	0.746(2)	0.148(8)
C(1)	0.2336(10)	-0.179(2)	0.699(1)	0.048(5)
C(2)	0.2769(9)	-0.187(2)	0.782(1)	0.044(5)
C(3)	0.2902(9)	-0.334(2)	0.843(1)	0.041(5)
C(4)	0.350(1)	-0.343(2)	0.911(1)	0.059(6)
C(5)	0.361(1)	-0.478(3)	0.968(1)	0.068(6)
C(6)	0.313(1)	-0.610(3)	0.958(1)	0.066(6)
C(7)	0.256(1)	-0.604(2)	0.895(2)	0.067(6)
C(8)	0.2447(10)	-0.462(2)	0.837(1)	0.052(5)
C(9)	0.1389(8)	-0.066(2)	0.509(1)	0.042(5)
C(10)	0.1498(9)	-0.052(2)	0.405(1)	0.048(5)
C(11)	0.1022(10)	-0.122(3)	0.340(1)	0.055(6)
C(12)	0.040(1)	-0.201(2)	0.368(2)	0.063(7)
C(13)	0.0290(9)	-0.217(2)	0.480(2)	0.060(6)
C(14)	0.0772(8)	-0.152(2)	0.545(1)	0.047(5)
C(15)	-0.014(2)	-0.277(3)	0.293(2)	0.11(1)
C(16)	0.477(2)	0.085(8)	0.042(3)	0.23(3)

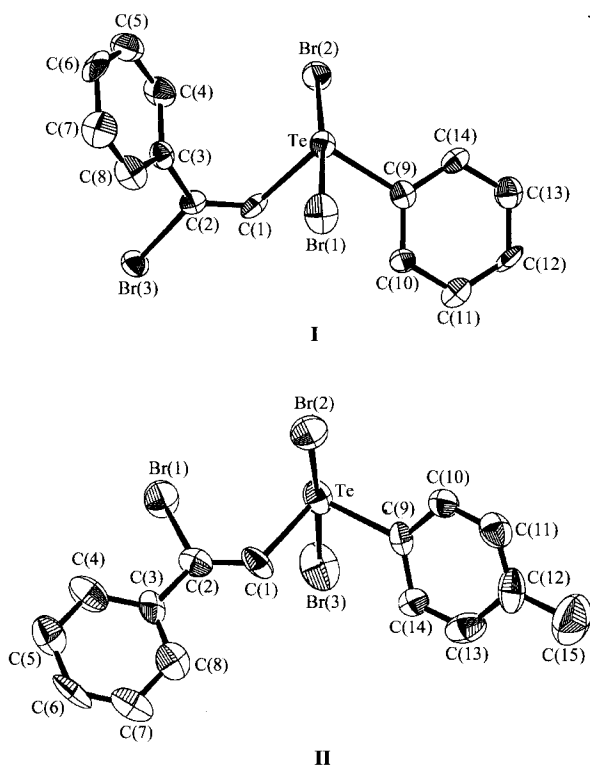


Fig. 1 Molecular structures of the compounds **I** and **II** (Displacement ellipsoids are at the 30% probability level).

The bonding in the molecule, either *E*- or *Z*-type

configuration, is consistent with the prediction of classical bonding models for AB_4E molecules.⁵ Two Br atoms are axial with the Br—Te—Br angles of $176.49(4)^\circ$ for **I** and $175.19(9)^\circ$ for **II**, whereas two C atoms are placed in equatorial position with the C—Te—C angles of $94.7(3)^\circ$ for **I** and $95.8(7)^\circ$ for **II** which are smaller than the average value of 99° found in these species. The lone pair of electrons occupies one of the equatorial sites. The bond lengths of Te—Br are 0.2718(1) and 0.2640(1) nm for **I** and 0.2713(2) and 0.2631(2) nm for **II**, respectively. As expected for trigonal bipyramidal configuration, the axial bonds are 0.021, 0.013 nm for **I** and 0.020, 0.012 nm for **II** longer than the sum of the normal covalent radii, 0.251 nm.⁶ The Te—C bond distances in both structures are nearly the same and the average Te—C bond of 0.211 nm is in good agreement with the values found for most Te^{IV} —C bonds.^{7,8} The C(2)—C(3) bond lengths in both structures are 0.147(2) nm which is shorter than the sum of the corresponding single-bond radii, supposing the delocalization of electronic density occurs in the conjugated system starting from the C(1) atom to phenyl rings. The fact that in both compounds the phenyl rings with the atoms of C(1) and C(2) reside in a perfect plane is further evidence.

Table 3 Selected bond distances (nm) and angles ($^\circ$) for compounds **I** and **II**

Compound I		Compound II	
Distance			
Te—Br(1)	0.2640(1)	Te—Br(2)	0.2715(2)
Te—Br(2)	0.2718(1)	Te—Br(3)	0.2631(2)
Te—C(1)	0.2099(9)	Te—C(1)	0.211(2)
Te—C(9)	0.2112(8)	Te—C(9)	0.210(1)
Br(3)—C(2)	0.1917(9)	Br(1)—C(2)	0.190(2)
C(1)—C(2)	0.132(1)	C(1)—C(2)	0.132(2)
C(2)—C(3)	0.147(1)	C(2)—C(3)	0.147(2)
Angle			
Br(1)—Te—Br(2)	176.49(4)	Br(2)—Te—Br(3)	175.21(8)
Br(1)—Te—C(1)	89.4(2)	Br(2)—Te—C(1)	86.5(5)
Br(1)—Te—C(9)	91.5(2)	Br(2)—Te—C(9)	89.9(4)
Br(2)—Te—C(1)	87.4(2)	Br(3)—Te—C(1)	88.8(5)
Br(2)—Te—C(9)	90.0(2)	Br(3)—Te—C(9)	90.9(4)
C(1)—Te—C(9)	94.7(3)	C(1)—Te—C(9)	95.5(6)
Te—C(1)—C(2)	120.1(6)	Te—C(1)—C(2)	123(1)
Br(3)—C(2)—C(1)	116.9(6)	Br(1)—C(2)—C(1)	117(1)
Br(3)—C(2)—C(3)	114.4(6)	Br(1)—C(2)—C(3)	118(1)
C(1)—C(2)—C(3)	128.7(8)	C(1)—C(2)—C(3)	125(2)
C(2)—C(3)—C(4)	120.2(8)	C(2)—C(3)—C(4)	120(2)
C(2)—C(3)—C(8)	122.0(8)	C(2)—C(3)—C(8)	121(2)
Te—C(9)—C(10)	120.1(6)	Te—C(9)—C(10)	119(1)
Te—C(9)—C(14)	118.4(6)	Te—C(9)—C(14)	122(1)

In both structures, the dihedral angles between the least-squares planes of the phenyl rings are 36.03° for **I** and 52.50° for **II**, respectively. The bond lengths and angles in the organic moiety are within the expected range of value. The fact that the stereoselectivity of the reaction (Scheme 1) is related to polarity of solvent employed shows *E*- or *Z*-type configuration passes through tellurium ion intermediate or four-membered cyclic transition state.

References

- 1 Chieffi, A.; Comasseto, J. V. *Tetrahedron Lett.* **1994**, 4063.
- 2 Ogawa, A.; Tsuboi, Y.; Obagashi, R.; Yokoyama, K.; Ryū, I.; Sonoda, N. *J. Org. Chem.* **1994**, *59*, 1600.
- 3 Petragani, N.; Comasseto, J. V. *Synthesis* **1991**, 793.
- 4 Huang, X.; Wang, Y. P. *Tetrahedron Lett.* **1996**, *37*, 7417.
- 5 Gillespie, R. J. *Molecular Geometry*, Van Zostrand Reinhold, London, **1972**.
- 6 Pauling, L. *The Nature of the Chemical Bond*, 3rd. ed., Cornell Univ. Press, NY. Ithaca, **1960**.
- 7 DE Matheus, M.; Torres, L.; Piniella, J. F.; Brianso, J. L.; Miravittles, C. *Acta Cryst.* **1991**, *C47*, 703.
- 8 Zukerman-Schpector, J.; Castellano, E. E.; Oliva, G.; Comasseto, J. V.; Stefani, H. A. *Acta Cryst.* **1991**, *C47*, 960.

(E200010222 SONG, J.P.; LING, J.)