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Tellurium-Capped Carbon Rods: Syntheses and Electronic and Structural Properties

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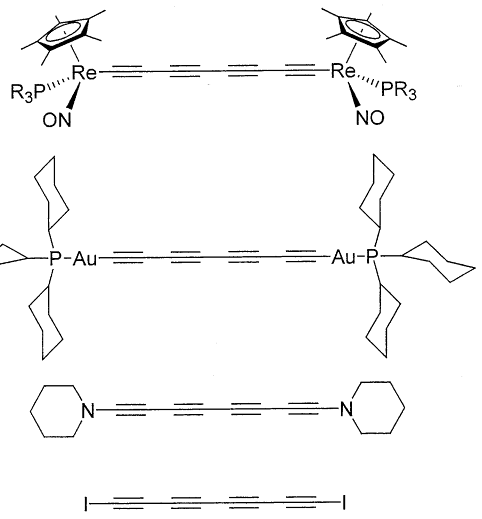
The synthesis of bis(methyltelluro)alkynes with two (**2**), three (**3**), and four (**4**) alkyne units was achieved. The key step was the reaction of the corresponding bis(trimethylsilyl)-alkynes **10**−**12** with methyllithium, tellurium, and methyliodide in a one-pot reaction. The structures of **2**−**4** as well as that of bis(methyltelluro)acetylene (**1**) were investigated in the solid state. All four samples showed C_2 symmetry in the solid state. For **1**−**4** we found relatively short Te···Te contacts of two neighbors, giving rise to a zigzag arrangement between the Te centers and forming stacks of molecules. The He(I) and He(II) photoelectron spectra of **1** as well as the UV/vis spectra of **1**−**4** are reported and discussed.

Introduction

Chart 1



The first syntheses of polyalkynes were initiated by natural product chemistry in the 1950s.[1] Since that time the chemistry of polyalkynes has gained momentum due to a number of new protecting groups,[2,3] new or improved C−C coupling reactions,[4,5] and new techniques to generate triple bonds.[5−7] Frequently used groups to protect the ends were *tert*-butyl,[8] aryl,[3] and trialkylsilyl groups,[2] various metallocenes,[9,10] and metal fragments containing Re,[11] Mo,[12] W,[12] Fe,[13] Ru,[14] Pt,[15] and Au[16] which are directly bound to the alkynes (Chart 1). The progress in this area was also spurred by the search for new materials such as carbon networks.[17] Among the various end groups, those containing electron-rich main group atoms are rare. Examples are bis(dialkylamino)alkynes[18] and dihaloalkynes with bromine[11b] and iodine[19] as termini (Chart 1).

In the course of our in-depth study of van der Waals interactions between chalcogen atoms connected with

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(1) (a) Bohlmann, F. *Angew. Chem.* **1955**, *67*, 389−394. (b) Bohlmann, F.; Herbst, P.; Gleinig, H. *Chem. Ber.* **1961**, *94*, 948−957.

(2) Eastmond, R.; Johnson, T. R.; Walton, D. R. M. *Tetrahedron* **1972**, *28*, 4601−4616.

(3) Gibtner, T.; Hampel, F.; Gisselbrecht, J.-P.; Hirsch, A. *Chem. Eur. J.* **2002**, *8*, 408−432, and references therein.

(4) (a) Chodkiewicz, W.; Cadiot, P. *Compt. Rend.* **1955**, *241*, 1055−1057. (b) Chodkiewicz, W. *Ann. Chim. (Paris)* **1957**, *2*, 819−869.

(5) (a) Rubin, Y.; Lin, S. S.; Knobler, C. B.; Anthony, J.; Boldi, A. M.; Diederich, F. *J. Am. Chem. Soc.* **1991**, *113*, 6943−6949. (b) Siemsen, P.; Livingston, R. C.; Diederich, F. *Angew. Chem.* **2000**, *112*, 2740−2767; *Angew. Chem., Int. Ed.* **2000**, *39*, 2632−2657.

(6) (a) Lalezari, I.; Shafiee, A.; Yalpani, M. *Angew. Chem.* **1970**, *82*, 484; *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 464−465. (b) Tobe, Y.; Fujii, T.; Naemura, K. *J. Org. Chem.* **1994**, *59*, 1236−1237. (c) Eisler, S.; Tykwinski, R. R. *J. Am. Chem. Soc.* **2000**, *122*, 10736−10737.

(7) (a) Grösser, T.; Hirsch, A. *Angew. Chem.* **1993**, *105*, 1390−1392; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1138−1141. (b) Schermann, G.; Grösser, T.; Hampel, F.; Hirsch, A. *Chem. Eur. J.* **1997**, *3*, 1105−1112.

(8) Jones, E. R. H.; Lee, H. H.; Whiting, M. C. *J. Chem. Soc.* **1960**, 3483−3489.

(9) (a) Altmann, M.; Enkelmann, V.; Bunz, U. H. F. *Chem. Ber.* **1996**, *129*, 269−273. (b) Bunz, U. H. F.; Roidl, G.; Altmann, M.; Enkelmann, V.; Shimizu, K. D. *J. Am. Chem. Soc.* **1999**, *121*, 10719−10726.

(10) (a) Classen, J.; Gleiter, R.; Rominger, F. *Eur. J. Inorg. Chem.* **2002**, 2040−2046. (b) Adams, R. D.; Qu, B.; Smith, M. D. *Organometallics* **2002**, *21*, 3867−3872.

(11) (a) Brady, M.; Weng, W.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1994**, 2655−2656. (b) Dembinski, R.; Bartik, T.; Bartik, B.; Jaeger, M.; Gladysz, J. A. *J. Am. Chem. Soc.* **2000**, *122*, 810−822. (c) Meyer, W. E.; Amoroso, A. J.; Horn, C. R.; Jaeger, M.; Gladysz, J. A. *Organometallics* **2001**, *20*, 1115−1127.

(12) (a) Bruce, M. I.; Ke, M.; Low, P. J. *J. Chem. Soc., Chem. Commun.* **1996**, 2405−2406. (b) Bruce, M. I.; Ke, M.; Low, P. J.; Skelton, B. W.; White, A. H. *Organometallics* **1998**, *17*, 3539−3549.

(13) (a) Coat, F.; Lapinte, C. *Organometallics* **1996**, *15*, 477−479. (b) Akita, M.; Chung, M.-C.; Sakurai, A.; Sugimoto, S.; Terada, M.; Tanaka, M.; Moro-oka, Y. *Organometallics* **1997**, *16*, 4882−4888.

(14) (a) Bruce, M. I.; Kelly, B. D.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **2000**, *604*, 150−156. (b) Wong, K.-T.; Lehn, J.-M.; Peng, S.-M.; Lee, G.-H. *J. Chem. Soc., Chem. Commun.* **2000**, 2259−2260.

(15) (a) Peters, T. B.; Bohling, J. C.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1999**, *18*, 3261−3263. (b) Mohr, W.; Stahl, J.; Hampel, F.; Gladysz, J. A. *Inorg. Chem.* **2001**, *40*, 3263−3264.

(16) Lu, W.; Xiang, H.-F.; Zhu, N.; Che, C.-M. *Organometallics* **2002**, *21*, 2343−2346.

(17) (a) Wan, W. B.; Brand, S. C.; Pak, J. J.; Haley, M. M. *Chem. Eur. J.* **2000**, *6*, 2044−2052. (b) Wan, W. B.; Haley, M. M. *J. Org. Chem.* **2001**, *66*, 3893−3901.

(18) Faul, D.; Himbert, G. *Chem. Ber.* **1988**, *121*, 1367−1369.

(19) (a) Gao, K.; Goroff, N. S. *J. Am. Chem. Soc.* **2000**, *122*, 9320−9321. (b) Hlavatý, J.; Kavan, L.; Štícha, M. *J. Chem. Soc., Perkin Trans. 1* **2002**, 705−706.

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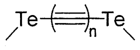
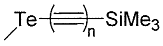
an sp center[20] we gained interest in the structures and properties of bis(methyltelluro)alkynes. The first member of this series, R−Te−C≡C−Te−R, with R = alkyl[21] and aryl[22] has been described in the literature, but higher members are unknown. We report in this paper the syntheses and properties of the bis(methyltelluro)alkynes **1**−**4**.

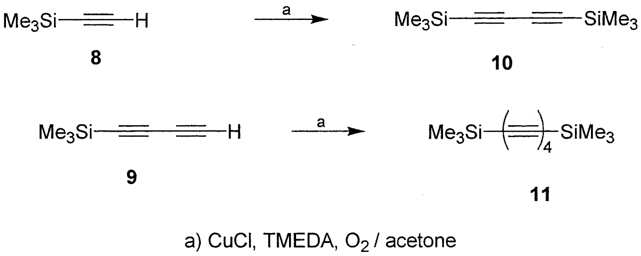

n=1, 2, 3, 4
1, 2, 3, 4


n=1, 2, 3
5, 6, 7

Results and Discussion

Syntheses. Our synthesis of **2**−**4** commenced with the preparation of the corresponding bis(trimethylsilyl)alkynes which were described in the literature.[2] To obtain the 1,3-butadiyne and the 1,3,5,7-octatetrayne derivatives **10** and **11**, respectively (Scheme 1), we started with the monosilylated alkynes **8** and **9**, which were coupled by applying the Eglinton protocol using the CuCl·TMDA complex in molar amounts in the presence of oxygen.[23] To obtain 1,6-bis(trimethylsilyl)hexa-1,3,5-triyne (**15**) we first generated hexa-2,4-diyne-1,6-diol (**13**) by oxidative coupling of propargylic alcohol (**12**) (Scheme 2). The tosylate **14** was treated with *n*-butyllithium (*n*-BuLi) and trimethylsilyl chloride to yield **15**.

Scheme 1



The transformation of **10**, **11**, and **15** to the corresponding bis(methyltelluro)alkynes **2**−**4** could be achieved in a one-pot reaction by first treating the silylated alkynes with methyllithium in the presence of lithium bromide followed by insertion of tellurium in the carbon−lithium bond and then electrophilic capture by methyl iodide (Scheme 3).[24] The resulting bis(methyltelluro)alkynes which could be obtained in 5−46% yield were brown-red colored solids, sensitive to light. As side products we isolated the monotelluroalkynes **5**−**7**.

Structural Investigations. Our main impetus for carrying out this project was the structure elucidation of **1**−**4** in the solid state. Recently we found that van der Waals interactions between chalcogen centers may lead to columnar or tubular structures when the chalcogen atoms were incorporated into fairly rigid systems.[20] Fortunately, we were able to grow single crystals for all four compounds. In Figure 1 we show the molecular structures of **1**−**4** in the solid state.

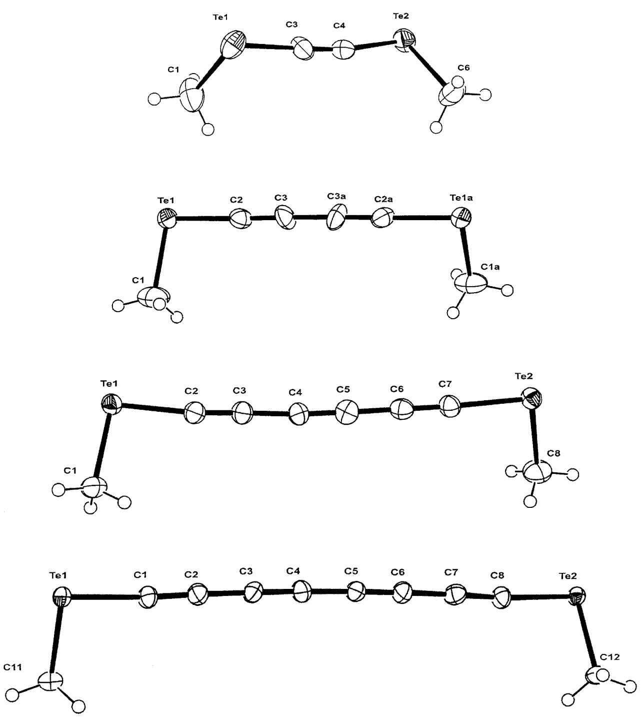


Figure 1. ORTEP plot (50% ellipsoid probability) of the molecular structures of **1**−**4** in the solid state (from top to bottom).

In Table 1 we compare relevant bond lengths, bond angles, and torsional angles of **1**−**4**. We find a large variation of the torsional angles between the CH_3−Te bonds; they vary between 44° (**3**) and 102° (**1**). The C(sp)−Te−CH_3 angles show values between 93° and 95°.

As Figure 1 shows the Te−(C≡C)$_n$−Te chain is not linear. Deviations of 2−6° per atom from linearity are encountered. As anticipated, the bond lengths between the sp centers alternate strongly between 1.19 and 1.20 Å for the triple bonds and from 1.36 to 1.39 Å for the sp−sp single bonds.

DFT calculations[25] (B3LYP/6-311G* for C, H and SDB-cc-pVTZ (with ECP) for Te)[26] on **1**−**4** reveal a C_2-symmetric global minimum showing a torsional angle of the methyl groups of about 90−92°. For the rotational barrier from the global minimum to its mirror image via the C_{2h}-symmetric transition state we calculated the following barriers: 11.5 kJ/mol (**1**), 6.9 kJ/mol (**2**), 4.3 kJ/mol (**3**), 2.8 kJ/mol (**4**). The decrease of the activation energy with increasing chain length is anticipated.

All bis(methyltelluro)alkynes (**1**−**4**) that were investigated show relatively short contacts between the tellurium centers. In Figures 2, 3, and 4 we show in a top and a side view the arrangements of **2**, **3**, and **4** in the solid state. As already discussed for **2**, we find as a

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(20) (a) Werz, D. B.; Staeb, T. H.; Benisch, C.; Rausch, B. J.; Rominger, F.; Gleiter, R. *Org. Lett.* **2002**, *4*, 339−342. (b) Werz, D. B.; Gleiter, R.; Rominger, F. *J. Am. Chem. Soc.* **2002**, *124*, 10638−10639.

(21) Gedridge, R. W., Jr.; Higa, K. T.; Harris, D. C.; Nissan, R. A.; Nadler, M. P. *Organometallics* **1989**, *8*, 2812−2816.

(22) Farran, J.; Torres-Castellanos, L.; Alvarez-Larena, A.; Piniella, J. F.; Capparelli, M. V. *J. Organomet. Chem.* **2002**, *654*, 91−99.

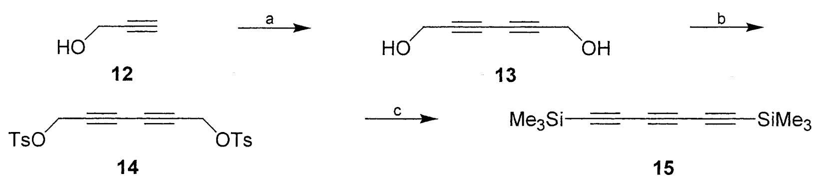
(23) (a) Behr, O. M.; Eglinton, G.; Galbraith, A. R.; Raphael, R. A. *J. Chem. Soc.* **1960**, 3614−3625. (b) Eglinton, G.; McCrae, W. *Adv. Org. Chem.* **1963**, *4*, 225−228.

(24) Brandsma, L. *Preparative Acetylenic Chemistry*, 2nd ed.; Elsevier: Amsterdam, 1988.

(25) (a) Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: Oxford, 1989. (b) Koch, W.; Holthausen, M. C. *A Chemist's Guide to Density Functional Theory*; Wiley-VCH: Weinheim, 2000.

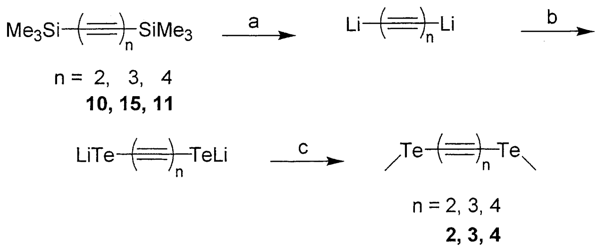
(26) (a) Martin, J. M. L.; Sundermann, A. *J. Chem. Phys.* **2001**, *114*, 3408−3420. (b) Bergner, A.; Dolg, M.; Kuechle, W.; Stoll, H.; Preuss, H. *Mol. Phys.* **1993**, *80*, 1431−1441.

Scheme 2



a) CuCl, NH$_4$Cl, O$_2$ / EtOH
b) TsCl / KOH
c) *n*-BuLi, Me$_3$SiCl

Scheme 3



a) MeLi / LiBr
b) Te
c) MeI

Table 1. Bond Lengths (Å), Bond Angles (deg), and Torsional Angles (deg) of 1−4

	Compound **1**[a]		
Te1−C3	2.041(12)	C3−Te1−C1	95.4(4)
Te1−C1	2.148(11)	C4−Te2−C6	94.3(5)
Te2−C4	2.045(12)	C4−C3−Te1	176.1(11)
Te2−C6	2.143(11)	C3−C4−Te2	168.7(10)
C3−C4	1.195(13)	C1−Te1−Te2−C6	101.8(5)
	Compound **2**		
Te1−C2	2.03(2)	C2−Te1−C1	94.2(6)
Te1−C1	2.17(2)	C3−C2−Te1	176(2)
C2−C3	1.22(3)	C2−C3−C3a	178(3)
C3−C3a	1.35(3)	C2−Te1−Te1a−C2a	53(1)
	Compound **3**		
Te1−C2	2.048(6)	C2−Te1−C1	93.5(3)
Te1−C1	2.142(6)	C7−Te2−C8	94.7(3)
Te2−C7	2.036(6)	C3−C2−Te1	174.0(6)
Te2−C8	2.141(7)	C2−C3−C4	176.9(7)
C2−C3	1.187(9)	C5−C4−C3	176.6(7)
C3−C4	1.398(9)	C4−C5−C6	178.3(7)
C4−C5	1.187(9)	C7−C6−C5	177.7(7)
C5−C6	1.377(9)	C6−C7−Te2	177.8(6)
C6−C7	1.201(9)	C1−Te1−Te2−C8	44.5(3)
	Compound **4**		
Te1−C1	2.033(4)	C1−Te1−C11	93.76(19)
Te1−C11	2.146(5)	C8−Te2−C12	93.80(19)
Te2−C8	2.030(5)	C2−C1−Te1	176.5(4)
Te2−12	2.147(5)	C1−C2−C3	178.7(5)
C1−C2	1.208(6)	C4−C3−C2	178.8(5)
C2−C3	1.379(7)	C3−C4−C5	178.8(5)
C3−C4	1.202(6)	C6−C5−C4	178.6(6)
C4−C5	1.361(7)	C5−C6−C7	178.6(5)
C5−C6	1.194(6)	C8−C7−C6	178.3(5)
C6−C7	1.383(7)	C7−C8−Te2	175.2(4)
C7−C8	1.221(7)	C1−Te1−Te2−C11	45.9(2)

[a] 2.5 independent molecules exist in the unit cell; the values given in the table are only for the best of them. For the numbering see Figure 1.

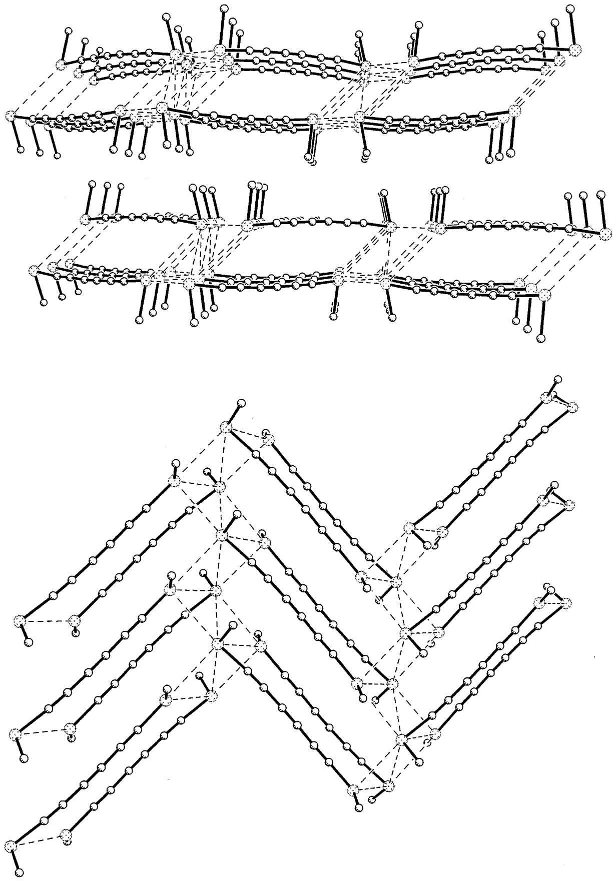


Figure 2. Top view and side view of the structure of **3** in the crystal. The short distances between the Te centers are indicated.

Table 2. Distances (Å) within a Zigzag Arrangement of Two Stacks and Distances within a Stack for Comparison of 2−4

compound	distances within a zigzag arrangement of tellurium atoms between two stacks		distance within a stack
2	3.74	3.82	4.46
3	3.69	3.84	5.53
	4.07	4.07	5.53
4	3.73	3.73	4.45
	3.88	3.88	4.45

common building motif that the tellurium centers form short contacts to those of two neighbors, giving rise to a zigzag arrangement between the tellurium centers.[20] This is best seen from the side view. As a result, the C_2-symmetric chains are packed on top of each other. Whereas the distances within the zigzag arrangement are shorter than the van der Waals distances between two tellurium atoms (4.4 Å),[27] the distances between the chains within a stack are relatively wide (4.45 Å (**2**), 5.53 Å (**3**), and 4.45 Å (**4**)). In Table 2 the distances within a zigzag arrangement of tellurium atoms between two stacks and the distances within a stack are listed for **2**−**4**.

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(27) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1973.

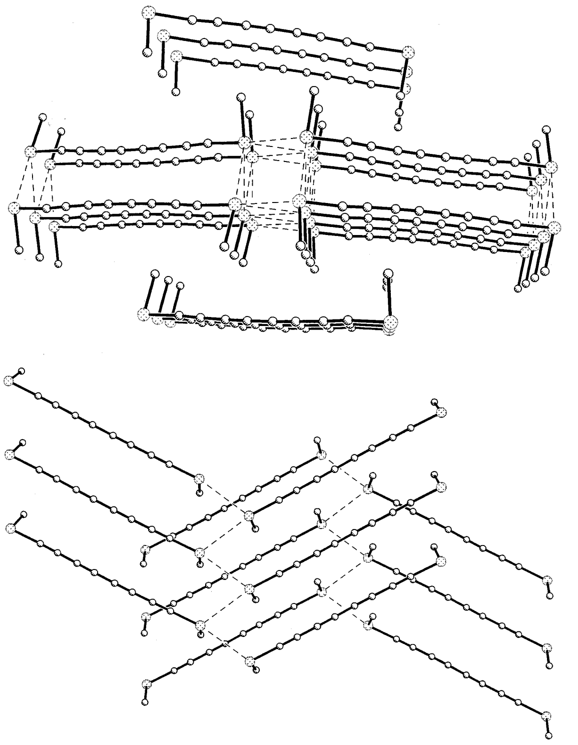

Figure 3. Top view and side view of the structure of **4** in the crystal. The short distances between the Te centers are indicated.

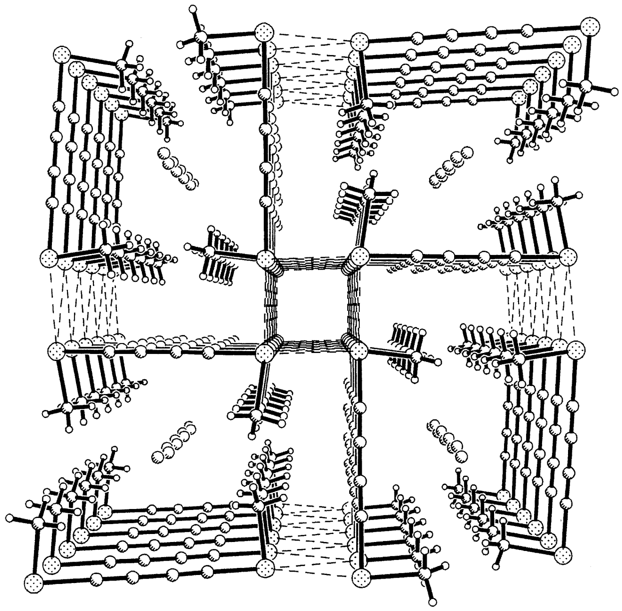

Figure 4. Top view of the structure of **2** indicating the included *n*-hexane molecules and the close Te···Te contacts.

In the case of **3** the tellurium atoms of four piles of molecules form a rhomboedric arrangement (Figure 2), whereas the four piles of **4** form a rectangle with almost equal distances (Figure 3). In the solid state of **3** and **4** the space left by the methyl groups of one pile is filled by methyl groups of two neighboring piles to avoid any holes.

For **2** we met a different situation. When this substance was recrystallized from *n*-hexane, the methyl groups of two piles form a rectangular box (~7 Å × 7 Å) which houses *n*-hexane. In the X-ray structure analysis the solvent appears as disordered electron density. The boxes are held together by short Te···Te interactions as shown in Figure 4.

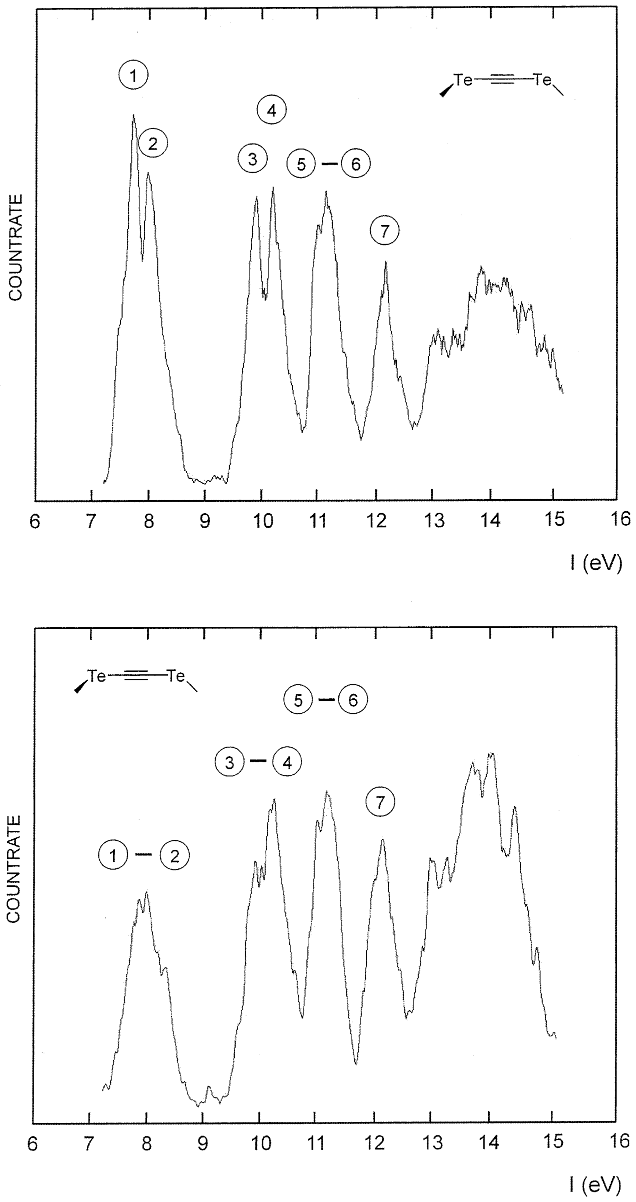

Figure 5. Photoelectron spectra of **1**: He(I) (top) and He(II) (bottom).

By examining the directionality of the Te···Te contacts in our examples we found that the 5p lone pair of the tellurium coincides in many cases with the direction of a Te–C bond of a neighboring molecule. Thus, we assume that the energy gain favoring this kind of solid state structure is a result of the interplay of the Te 5p lone pair and the unoccupied Te–C σ^* orbital. This kind of interaction was also encountered in other chalcogen systems.[20,28]

Spectroscopic Investigations. To understand the electronic structures of **1**–**4**, we have investigated the photoelectron spectra of **1** and the electronic absorption spectra of **1**–**4**.

The He(I) and He(II) photoelectron (PE) spectra of **1** are shown in Figure 5. We recognize six peaks below

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[28] Glusker, J. P. *Top. Curr. Chem.* **1998**, *198*, 1–56. (b) Rosenfield, R. E.; Parthasarathy, R.; Dunitz, J. D. *J. Am. Chem. Soc.* **1977**, *99*, 4860–4862.

Table 3. Listing of the Vertical Ionization Energies, $I_{v,j}$, Calculated Orbital Energies, ϵ_j, Assignments, and Relative Band Intensities from He(I) and He(II) PE Spectra of 1

band	$I_{v,j}$[a]	assignment[b]	$-\epsilon_j$[a]	relative He(I)	relative He(II)
1	7.8	11a [n(p)]	8.05	1.4[c]	0.9[c]
2	8.0	10b [n(p)]	8.06		
3	10.0	10a [π,n(sp^n)]	10.80	1.2[c]	1.2[c]
4	10.3	9b [π,n(sp^n)]	10.81		
5	11.1	9a [π,n(sp^n)]	12.21	1.0[c]	1.0[c]
6	11.3	8b [π,n(sp^n)]	12.32		
7	12.3	8a [σ]	13.84	0.6[c]	0.8[c]

[a] The ionization energies and orbital energies are given in eV. [b] The assignment of the bands to MOs is based on the assumption of C_2 symmetry. The numbering refers to the results of the HF calculation based on the geometry of lowest energy. [c] Average value, setting the intensity of the third peak to 1.0.

13 eV in the He(I) spectrum. We have assigned seven transitions to these peaks, based on the areas below the peak envelopes. In the He(II) spectrum the bands overlap more, giving rise to only four peaks. This is due to the lower count rate (ca. 180−200 cps) compared to the He(I) spectrum (400 cps), which results in a lower resolution.

To assign the bands to various ionization events, we assume the validity of Koopmans' theorem ($-\epsilon_j = I_{v,j}$).[29] This assumption allows the correlation of the measured vertical ionization energy ($I_{v,j}$) with the calculated orbital energy (ϵ_j). To check our assignment experimentally, we make use of the observation that the intensity of a PE band depends on the photon wavelength. As a rule, He(I) photons favor the ejection from diffuse orbitals, whereas He(II) photons favor the ejection from contracted orbitals.[30] Bands associated with ionizations from the lone pair of chalcogen atoms are considerably enhanced in the He(I) PE spectra relative to those bands that originate from carbon π-systems.[30a]

The relative intensities of the He(I) and the He(II) PE bands are listed in Table 3. A comparison between the intensities shows a lower intensity for bands 1 and 2 of the He(II) spectra, indicating that the corresponding wave function has high 5p character. A comparison between experiment ($I_{v,j}$) and calculation (ϵ_j) suggests the assignment given in Table 3. The first two bands originate from MOs that are mainly localized at the Te atoms, and the other bands originate from π orbitals mixing with n(sp^n) orbitals of Te (3−6) or σ orbitals (7) of the alkyne unit. In Figure 6 the HOMO (n-type), HOMO-2 (π-type), and HOMO-6 (σ-type) are shown.

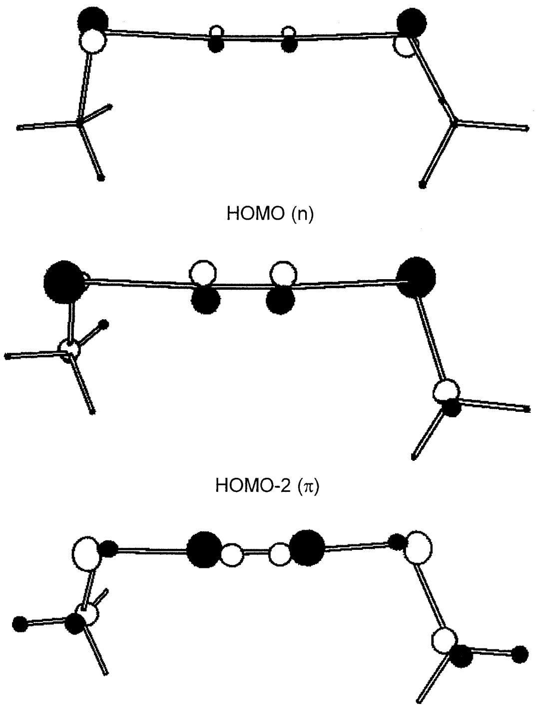

Figure 6. Schematic plot of HOMO (n), HOMO-2 (π), and HOMO-6 (σ) of **1**.

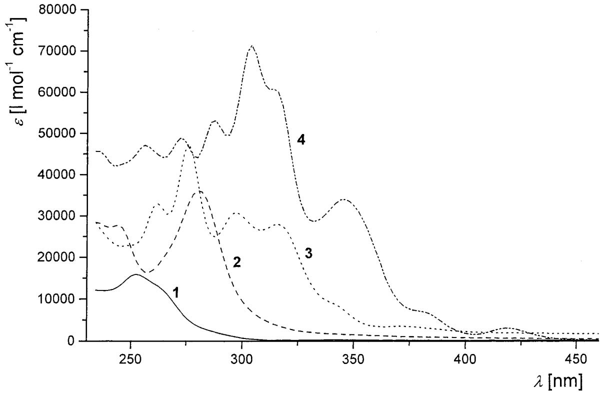

Figure 7. Electronic absorption spectra of **1**−**4** in dichloromethane as solvent.

The electronic spectra of polyalkynes have been used from the beginning of their chemistry to characterize them qualitatively.[1] A detailed analysis of the UV/vis spectra of the unsubstituted polyalkynes revealed two types of bands: at shorter wavelength the intensive $^1\Sigma_g^+ \rightarrow {}^1\Sigma_u^+$ transition and at longer wavelength the "forbidden" $^1\Sigma_g^+ \rightarrow {}^1\Delta_u$ transition of low intensity.[31,32] Although our samples have at most C_2 symmetry in solution, we still find for **3** and **4** bands at long wavelength with low intensity (Figure 7) and at shorter wavelength bands of higher intensity. This pattern of bands is in line with various linear alkynes substituted with bulky groups at the termini.[33] In our cases, however, the long-wavelength bands might also arise from n → π^* transitions due to the n-character of the HOMO (see Table 3).

In the ^{13}C NMR spectra of the bis(methyltelluro)alkynes an unusual solvent effect is observed. The alkynyl carbon atoms, bonded directly to tellurium, show in $CDCl_3$ a relative low-frequency resonance of about 40−44 ppm due to the "heavy-atom effect" of tellurium.[34] When the ^{13}C NMR spectra are recorded in DMSO-d_6, the peaks assigned to those carbon atoms

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(29) Koopmans, T. *Physica* **1934**, *1*, 104−113.

(30) (a) Price, W. C.; Potts, A. W.; Streets, D. G. In *Electron Spectroscopy*; Shirley, D. A., Ed.; North-Holland Publishing Company, 1972; pp 187−198. (b) Lichtenberger, D. L.; Kellog, G. E. *Acc. Chem. Res.* **1987**, *20*, 379−387. (c) Green, J. C. *Acc. Chem. Res.* **1994**, *27*, 131−137, and references therein.

(31) Kloster-Jensen, E. *Angew. Chem.* **1972**, *84*, 483−485; *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 438−440.

(32) (a) Kloster-Jensen, E.; Haink, H.-J.; Christen, H. *Helv. Chim. Acta* **1974**, *57*, 1731−1744. (b) Haink, H. J.; Jungen, M. *Chem. Phys. Lett.* **1979**, *61*, 319−322.

(33) Eastmond, R.; Walton, D. R. M. *Tetrahedron* **1972**, *28*, 4591−4599.

(34) Kaupp, M.; Malkina, O. L.; Malkin, V. G.; Pyykkö, P. *Chem. Eur. J.* **1998**, *4*, 118−126.

move 7−12 ppm to higher frequency. A similar effect in iodoalkynes was already investigated, both experimentally and theoretically.[35] We assume that an analogous Lewis acid−base interaction leads to the observed change: An oxygen lone pair of DMSO may act as a Lewis base, whereas the Te−C(sp) σ^* orbital may act as a Lewis acid.

Conclusion

We were successful in synthesizing bis(methyltelluro)alkynes with one to four alkyne units between the chalcogen centers. All four samples showed C_2 symmetry in the solid state with low rotational barriers. The investigation of the first member by PE spectroscopy revealed the Te 5p lone pairs as HOMO. In the solid state we detected for **1**−**4** strong intermolecular Te···Te interactions, which lead to the formation of stacks. When **2** was recrystallized from *n*-hexane, even a tubular structure including *n*-hexane was detected.

Experimental Section

General Methods. All reactions were conducted in oven-dried glassware under an argon atmosphere with magnetic stirring. The reaction flasks and columns for the purifications were wrapped in aluminum foil to minimize exposure to light. THF was dried with sodium/benzophenone and distilled under argon before use. Melting points are uncorrected. Materials used for column chromatography: silica gel 60 (Macherey-Nagel). NMR spectra were recorded at 300 or 500 MHz (^{1}H) and 75.5 or 125.8 MHz (^{13}C), respectively, using the solvent as internal standard. The IR spectra were recorded with a FT-IR instrument. The UV light absorption spectra were recorded using a Hewlett-Packard 8452 A spectrometer. The high-resolution mass spectra (HRMS) were recorded in the EI (70 eV) mode. Elemental analyses were carried out by the Mikroanalytisches Laboratorium der Universität Heidelberg. Trimethylsilylacetylene (**8**),[23] bis(trimethylsilyl)alkynes **10**,[36] **15**,[5] and **11**,[36] and bis(methyltelluro)acetylene (**1**)[21] were prepared according to literature methods.

The photoelectron spectra were recorded with a PS18 spectrometer (Perkin-Elmer) at 60−70 °C. The spectrometer was equipped with a Helectros lamp capable of giving both He(I) and He(II) radiation. Where a clear separation of bands was found, relative intensities were estimated by dividing the band areas. The spectra were recorded at least twice. The count rates for He(I) were 400 cps, for He(II) 180−200 cps. The spectra were calibrated with Ar and Xe. A resolution of 20 meV was obtained for the $^2P_{3/2}$ line of Ar.

General Procedure for the Preparation of 2−7. To a solution of bis(trimethylsilyl)alkyne in 150 mL of THF was added MeLi/LiBr in diethyl ether (1.5 M) dropwise at −78 °C over a period of 15 min. The solution was stirred for 3 h at −78 °C. After that, the reaction mixture was allowed to warm slowly to −20 °C. After cooling again to −40 °C, freshly ground tellurium powder (200 mesh) was added. The mixture was allowed to warm to room temperature and stirred overnight. A solution of methyl iodide in 50 mL of THF was added slowly at 0 °C. The solution was stirred for 1 h at 0 °C. A saturated NH_4Cl solution (100 mL) and 200 mL of hexane were added, the layers were separated, and the aqueous layer was extracted three times with hexane, yielding an orange solution. The organic layer was dried with anhydrous $MgSO_4$. After rotary evaporation the crude product was absorbed on Celite. The product was isolated by column chromatography {silica gel [3% NEt_3 (v/v)], *n*-hexane}.

2,7-Ditelluraocta-3,5-diyne (2). Starting materials: 1.80 g (9.26 mmol) of 1,4-bis(trimethylsilyl)buta-1,3-diyne, 14.3 mL (21.5 mmol) of MeLi/LiBr in diethyl ether, 3.08 g (24.1 mmol) of tellurium, and 3.04 g (21.5 mmol) of methyl iodide. Column chromatography afforded 201 mg (8%) of **6** and 154 mg (5%) of **2** as a brown solid: mp 49 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.17 (s, 6H, CH_3); ^{13}C NMR ($CDCl_3$, 125 MHz) δ −14.3 (TeCH$_3$), 40.6 (TeCC), 96.4 (TeCC); ^{13}C NMR (DMSO-d_6, 125 MHz) δ −12.3 (TeCH$_3$), 47.7 (TeCC), 94.2 (TeCC); ^{125}Te NMR (C_6D_6, 94.7 MHz) δ 199.9 (quart, $^2J_{\text{Te-H}} = 26$ Hz); IR (KBr) 2953, 1631 cm^{-1}; UV/vis (CH_2Cl_2, λ_{max}, nm (ϵ, M^{-1} cm^{-1}) 244 (27800), 280 (36100); (EI, 70 eV) *m/z* 333.9 (M$^+$, 51), 319.0 ([M − CH$_3$]$^+$, 81), 303.9 ([M − 2 CH$_3$]$^+$, 44); HRMS (EI) calcd for $C_6H_6{}^{126}Te^{128}Te$ 331.8547, found 331.8547. Anal. Calcd for $C_6H_6Te_2 \times 0.05C_6H_{14}$ (337.62): C, 22.41; H, 2.00. Found: C, 22.26; H, 1.99.

2,9-Ditelluradeca-3,5,7-triyne (3). Starting materials: 562 mg (2.58 mmol) of 1,6-bis(trimethylsilyl)hexa-1,3,5-triyne, 3.9 mL (5.9 mmol) of MeLi/LiBr in diethyl ether, 750 mg (5.9 mmol) of tellurium, and 840 mg (5.9 mmol) of methyl iodide. Column chromatography afforded 105 mg (14%) of **7** and 424 mg (46%) of **3** as a orange-brown solid: mp 58 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.20 (s, 6H, CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −14.3 (TeCH$_3$), 42.0 (TeCC), 64.1 (CC), 96.2 (CC); ^{13}C NMR (DMSO-d_6, 75 MHz) δ −12.0 (TeCH$_3$), 52.9 (TeCC), 62.8 (CC), 93.1 (CC); ^{125}Te NMR (C_6D_6, 94.7 MHz) δ 218.9 (quart, $^2J_{\text{Te-H}} = 27$ Hz); IR (KBr) 2928, 2129, 1635 cm^{-1}; UV/vis (CH_2Cl_2, λ_{max}, nm (ϵ, M^{-1} cm^{-1})) 262 (36900), 276 (53600), 298 (28900), 316 (30600), 342 (8200), 372 (2500); (EI, 70 eV) *m/z* 357.9 (M$^+$, 44), 342.8 ([M − CH$_3$]$^+$, 46), 328 ([M − 2 CH$_3$]$^+$, 92); HRMS (EI) calcd for $C_8H_6{}^{128}Te^{130}Te$ 359.8577, found 359.8559. Anal. Calcd for $C_8H_6Te_2$ (357.34): C, 26.89; H, 1.69. Found: C, 26.60; H, 1.80.

2,11-Ditelluradodeca-3,5,7,9-tetrayne (4). Starting materials: 145 mg (0.60 mmol) of 1,8-bis(trimethylsilyl)octa-1,3,5,7-tetrayne, 0.96 mL (1.44 mmol) of MeLi/LiBr in diethyl ether, 190 mg (1.49 mmol) of tellurium, and 211 mg (1.49 mmol) of methyl iodide. Column chromatography afforded 46 mg (20%) as a brown solid: mp 105 °C (explosion!); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.21 (s, 6H, CH_3); ^{13}C NMR (C_6D_6, 125 MHz) δ −15.4 (TeCH$_3$), 44.3 (TeCC), 64.8 (C), 65.1 (C), 97.1 (C); ^{13}C NMR (DMSO-d_6, 125 MHz) δ −11.8 (TeCH$_3$), 55.6 (TeCC), 62.5 (CC), 63.9 (C), 93.3 (CC); ^{125}Te NMR (C_6D_6, 94.7 MHz) δ 224.4 (quart, $^2J_{\text{Te-H}} = 26$ Hz); IR (KBr) 2929, 2160, 1634 cm^{-1}; UV/vis (CH_2Cl_2, λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 256 (47200), 274 (48900), 288 (53200), 304 (71500), 310 (61900), 332 (28600), 346 (34000), 378 (7200), 418 (3100); (EI, 70 eV) *m/z* 382 (M$^+$, 100), 367 ([M − CH$_3$]$^+$, 56), 352 ([M − 2 CH$_3$]$^+$, 82); HRMS (EI) calcd for $C_8H_6{}^{126}Te^{128}Te$ 379.8547, found 379.8545. Anal. Calcd for $C_{10}H_6Te_2$ (381.36): C, 31.50; H, 1.59. Found: C, 31.85; H, 1.93.

(Methyltelluro)(trimethylsilyl)acetylene (5). Instead of bis(trimethylsilyl)acetylene and MeLi/LiBr, 1.07 g (10.9 mmol) of trimethylsilylacetylene and 4.4 mL (11.0 mmol) of *n*-butyllithium (1.6 M in *n*-hexane), 1.45 g (11.4 mmol) of tellurium and 1.60 g (11.3 mmol) of methyl iodide were used. Column chromatography afforded 1.53 g (59%) as a yellow oil: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.17 (s, 9H, Si(CH_3)$_3$), 2.14 (s, 3H, TeCH_3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −14.8 (TeCH$_3$), 0.2 (Si(CH$_3$)$_3$), 61.9 (TeC), 120.5 (SiC); ^{13}C NMR (DMSO-d_6, 75 MHz); δ −13.3 (TeCH$_3$), 0.1 (Si(CH$_3$)$_3$), 70.0 (TeC), 117.2 (SiC); ^{125}Te NMR (C_6D_6, 94.7 MHz) δ 179.1 (quart, $^2J_{\text{Te-H}} =$ 25 Hz); IR (KBr) 2958, 2897, 2075, 1409, 1249 cm^{-1}; UV/vis (CH_2Cl_2, λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 240 (840), 342 (570); (EI, 70 eV) *m/z* 242 (M$^+$, 71), 227 ([M − CH$_3$]$^+$, 100), 212 ([M − 2 CH$_3$]$^+$, 53); HRMS (EI) calcd for $C_6H_{12}Si^{130}Te$ 241.9753, found 241.9780. Anal. Calcd for $C_6H_{12}SiTe$ (239.8): C, 30.05; H, 5.04. Found: C, 30.12; H, 5.28.

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(35) Rege, P. D.; Malkina, O. L.; Goroff, N. S. *J. Am. Chem. Soc.* **2002**, *124*, 370−371.

(36) Walton, D. R. M.; Waugh, F. *J. Organomet. Chem.* **1972**, *37*, 45−56.

Table 4. Crystal Data and Structure Refinement for Compounds 1, 2, 3, and 4

	1	**2**	**3**	**4**
empirical formula	$C_4H_6Te_2$	$C_6H_6Te_2$	$C_8H_6Te_2$	$C_{10}H_6Te_2$
fw	309.29	333.31	357.33	381.35
cryst syst	orthorhombic	tetragonal	monoclinic	monoclinic
space group	$Fdd2$	$I\bar{4}2d$	$P2_1/c$	$P2/c$
unit cell dimens				
a [Å]	15.3342(11)	20.1830(4)	8.9280(5)	10.7844(2)
b [Å]	83.836(6)	20.1830(4)	5.5321(3)	4.4450(1)
c [Å]	5.6583(4)	4.4590(1)	19.8301(11)	21.9525(4)
α [deg]	90	90	90	90
β [deg]	90	90	100.422(1)	96.343(1)
γ [deg]	90	90	90	90
Z	40	8	4	4
V [Å^3]	7274.1(9)	1816.39(7)	963.26(9)	1045.89(4)
D_{calc} [g/cm^3]	2.824	2.438	2.464	2.422
abs coeff	7.902	6.339	5.986	5.522
max./min. transmn	0.86/0.60	0.88/0.14	0.91/0.72	0.96/0.46
θ range for data coll. [deg]	1.94−25.70	2.02−23.33	2.09−27.49	1.87−27.45
index ranges	$-17 \le h \le 17$ $-97 \le k \le 100$ $-6 \le l \le 6$	$-22 \le h \le 22$ $-22 \le k \le 22$ $-4 \le l \le 4$	$-11 \le h \le 11$ $-7 \le k \le 7$ $-25 \le l \le 25$	$-13 \le h \le 13$ $-5 \le k \le 5$ $-28 \le l \le 28$
no. of reflns collected	11 611	6535	9453	10 124
no. of ind reflns	3160	659	2215	2378
no. of reflns obsd	2281	437	1632	1791
no. of obsd data/params	3160/131	659/42	2215/93	2378/111
goodness-of-fit on F^2	0.96	1.09	1.04	1.00
$R(F)$	0.037	0.045	0.035	0.028
$R_w(F^2)$	0.054	0.098	0.075	0.068
$(\Delta\rho)$max., $(\Delta\rho)$min. [e Å^{-3}]	1.70, −1.00	1.45, −0.64	1.30, −1.03	1.40, −0.95

(Methyltelluro)(trimethylsilyl)butadiyne (6). Yellow oil: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.18 (s, 9H, Si(C*H*$_3$)$_3$), 2.17 (s, 3H, TeC*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz) δ −14.7 (Te*C*H$_3$), −0.2 (Si(*C*H$_3$)$_3$), 38.4 (Te*C*), 87.4 (*C*), 88.3 (*C*), 96.0 (*C*); ^{13}C NMR (DMSO-d_6, 75 MHz); δ −12.5 (Te*C*H$_3$), −0.7 (Si(*C*H$_3$)$_3$), 48.6 (Te*C*), 85.5 (*C*), 89.0 (*C*), 93.2 (*C*); ^{125}Te NMR (C_6D_6, 94.7 MHz) δ 205.3 (quart, $^2J_{Te-H} = 26$ Hz); IR (KBr) 2959, 2897, 2195, 2138, 2055, 1633, 1410, 1251 cm^{-1}; UV/vis (CH_2Cl_2, λ_{max}, nm (ε, M^{-1} cm^{-1})): 242 (7400), 272 (950), 288 (870), 306 (660); (EI, 70 eV) *m*/*z* 266 (M$^+$, 97), 251 ([M − CH$_3$]$^+$, 100), 236 ([M − 2 CH$_3$]$^+$, 65); HRMS (EI) calcd for $C_8H_{12}Si^{130}Te$ 265.9771, found 265.9761. Anal. Calcd for $C_8H_{12}SiTe$ (263.8): C, 36.42; H, 4.58. Found: C, 36.50; H, 4.59.

(Methyltelluro)(trimethylsilyl)hexatriyne (7). Brown oil: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.20 (s, 9H, Si(C*H*$_3$)$_3$), 2.20 (s, 3H, TeC*H*$_3$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ -14.5 (Te*C*H$_3$), 0.0 (Si(*C*H$_3$)$_3$), 40.4 (Te*C*), 61.9 (*C*), 64.1 (*C*), 87.9 (*C*), 88.9 (*C*), 96.4 (*C*); ^{125}Te NMR (C_6D_6, 94.7 MHz) δ 218.2 (quart, $^2J_{Te-H} =$ 26 Hz); IR (KBr) 2959, 2161, 2139, 1410, 1250 cm^{-1}; UV/vis (CH_2Cl_2, λ_{max}, nm (ε, M^{-1} cm^{-1})): 240 (35700), 262 (24900), 276 (31900), 300 (8000), 312 (4600), 336 (4100), 360 (2300); (EI, 70 eV) *m*/*z* 290 (M$^+$, 64), 275 ([M − CH$_3$]$^+$, 52), 260 ([M − 2 CH$_3$]$^+$, 39); HRMS (EI) calcd for $C_{10}H_{12}Si^{130}Te$ 289.9771, found 289.9761.

X-ray Diffraction Analyses. The reflections were collected with a Bruker Smart CCD diffractometer (Mo Kα radiation, graphite monochromator). Intensities were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied using SADABS[37] based on the Laue symmetry of the reciprocal space. The structures were solved by direct methods. The structural parameters of the non-hydrogen atoms were refined anisotropically according to a full-matrix least-squares technique (F^2). The hydrogen atoms were calculated according to stereochemical aspects. Structure solution and refinement were carried out with the SHELXTL (5.10) software package.[37] ORTEP drawings were obtained using the ORTEP-3 for Windows program by L. Farrugia.[38] Table 4 contains the crystallographic data and details of the data collection and the refinement procedure. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: (internat.) + 44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk], on quoting the deposition numbers CCDC-195343 (**1**), -195071 (**2**), -195344 (**3**), and -195345 (**4**).

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Supporting Information Available: Crystal data for compounds **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[37] Sheldrick, G. M. *SHELXTL*; Bruker Analytical X-ray Division: Madison, WI, 1997.

[38] Farrugia, L. *ORTEP-3 for Windows*: A Version of Ortep-III with a Graphical User Interface (GUI). *J. Appl. Crystallogr.* **1997**, *72*, 565.