Synthesis, NMR Spectroscopic Investigation, and Crystal Structures of 1,3-Dihydro-2λ^4-benzotellurole-2,2-diyl Bis(diethyldithiocarbamate), $C_8H_8Te[S_2CNEt_2]_2$; *S*,*S'*-1,3-Dihydro-2λ^4-benzotellurole-2,2-diyl *O*,*O*,*O'*,*O'*-Tetraethyl Bis(dithiophosphate), $C_8H_8Te[S_2P(OEt)_2]_2$; and 1,3-Dihydro-2λ^4-benzotellurole-2,2-diyl Bis(*O*-ethyl xanthate), $C_8H_8Te[S_2COEt]_2$

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Abstract: The crystal and molecular structures of $C_8H_8Te(S_2CNEt_2)_2$ (**1**), $C_8H_8Te[S_2P(OEt)_2]_2$ (**2**), and $C_8H_8Te(S_2COEt)_2$ (**3**) have been determined; crystals of **1** are triclinic, space group $P\bar{1}$, $a = 9.453$ (1) Å, $b = 10.440$ (2) Å, $c = 13.641$ (2) Å, $\alpha = 68.28$ (1)°, $\beta = 76.74$ (1)°, $\gamma = 64.90$ (1)°, $Z = 2$; crystals of **2** are monoclinic, space group $P2_1/c$, $a = 10.856$ (1) Å, $b = 19.876$ (3) Å, $c = 12.206$ (2) Å, $\beta = 101.54$ (1)°, $Z = 4$; crystals of **3** are monoclinic, space group $C2/c$, $a = 17.166$ (1) Å, $b = 13.282$ (1) Å, $c = 16.349$ (1) Å, $\beta = 98.31$ (1)°, $Z = 8$. Each of the three structures shows evidence of a stereochemically active lone pair of electrons at the tellurium atom. **1** is monomeric with the tellurium atom coordinated by two benzylic carbon atoms and four sulfur atoms from two asymmetrically coordinated dithiocarbamate ligands which give an overall seven-coordinate geometry about the tellurium. **2** shows additional intermolecular Te–S interactions resulting in the formation of a one-dimensional polymer in which the Te atom is effectively eight coordinate. Additional intermolecular Te–S interactions in **3** result in dimer formation such that the tellurium atom is eight coordinate. The degree of association in the three complexes support the ligand donor strength order dtc > dtp > xan. Carbon-13, ^{31}P, and ^{125}Te NMR data of these and related compounds indicate that intramolecular monodentate–bidentate dithiolate exchange becomes slow on the NMR time scale at low temperature, and the structures inferred in solution approximate those observed directly in the solid state. Slow ligand exchange and "static gearing" result in observation of three conformational isomers for $C_8H_8Te(S_2CN^iPr_2)_2$ at low temperature. Conformational isomers are also observed in solutions of mixed-ligand complexes of the type $C_8H_8Te(S_2CNR_2)[S_2P(OR)_2]$, and the distribution of these isomers is solvent dependent.

In recent years there have been a number of reports of solid-state structures of tellurium(IV) complexes involving halogen or dithiocarbamate ligands.[3–6] Many of the complexes involving halogen ligands show the presence of a stereochemically active lone pair at tellurium, and most of these also show the presence of secondary bonds clustered about the region thought to be occupied by the lone pair. Tellurium(IV) complexes in which there is no evidence for stereochemical activity of a lone pair at tellurium, e.g., TeX_6^{2-} (X = Cl, Br),[5,6] $Te(dtc)_4$[7,8] (where dtc is a dithiocarbamate ligand), and $TeX_4(tmtu)_2$ (tmtu = tetramethylthiourea; X = Cl, Br),[9] do not show any secondary bonds. Apparently the factors which determine stereochemical activity may be finely balanced as is shown by the remarkable example of structural change in the solid state resulting in an "inert" electron pair eventually becoming active.[10] The origin of secondary bonding is not well understood. Furthermore, there is still a paucity of data regarding the stereochemistry of complexes in solution, and, in particular, it is not known whether secondary bonds have any influence in solution. As part of a contribution to the investigation of the stereochemistry and bonding in hypervalent tellurium compounds in the solid state and in solution, we have undertaken the synthesis and structural determinations of an extended range of new compounds with a variety of donor sets and now report solution NMR data and the crystal and molecular structures of $C_8H_8Te(Etdtc)_2$ (Etdtc = S_2CNEt_2) (**1**), $C_8H_8Te(Etdtp)_2$ (Etdtp = $S_2P(OEt)_2$) (**2**), and $C_8H_8Te(Etxan)_2$ (Etxan = S_2COEt) (**3**). We also report variable-temperature ^{13}C, ^{125}Te, and ^{31}P NMR data for a series of mixed-dithiolate complexes in solution.

Experimental Section

Materials. All solvents were AR grade or better.

Preparations. $C_8H_8Te(Etdtc)_2$ (**1**) was prepared by the reaction of $C_8H_8TeI_2$[11] (50 mmol) with NaEtdtc·3H_2O (100 mmol) in dichloromethane (100 cm^3). The solution was stirred overnight, filtered, and evaporated to dryness. Recrystallization from petroleum ether (40–60) gave colorless crystals suitable for X-ray crystallography: mp 150–151 °C. $C_8H_8Te(Etdtp)_2$ (**2**) and $C_8H_8Te(Etxan)_2$ (**3**) were prepared similarly by using KEtdtp and KEtxan, respectively. Yields were essentially quantitative. **2** and **3** were recrystallized from petroleum ether (40–60) to give pale yellow crystals (mp 127–130 °C dec) and colorless crystals (mp 105–106 °C), respectively. The analogous isopropyl derivatives of Etdtc, Etdtp, and Etxan complexes were similarly prepared by using the appropriate alkali metal salts of the dithiolate ligand.

Instrumentation. Infrared spectra were recorded on a Jasco A-302 spectrometer. NMR spectra were recorded with broad band decoupling on a JEOL FX 100 spectrometer. Temperatures were maintained by a NM 5471 controller calibrated with a platinum resistance thermometer. Carbon-13 spectra were generally recorded in CH_2Cl_2 at 25.0 MHz and

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Table I. Crystal Structure Data for $C_8H_8Te(S_2CNEt_2)_2$ (**1**), $C_8H_8Te[S_2P(OEt)_2]_2$ (**2**), and $C_8H_8Te(S_2COEt)_2$ (**3**)

compound	**1**	**2**	**3**
formula	$C_{18}H_{28}N_2S_4Te$	$C_{16}H_{28}O_4P_2S_4Te$	$C_{14}H_{18}O_2S_4Te$
M_r	528.26	602.18	474.12
cryst system	triclinic	monoclinic	monoclinic
space group	$P\bar{1}(C_i^1$; no. 2)	$P2_1/c(C_{2h}^5$; no. 4)	$C2/c(C_{2h}^6$; no. 15)
a, Å	9.453 (1)	10.856 (2)	17.166 (1)
b, Å	10.440 (2)	19.876 (3)	13.282 (1)
c, Å	13.641 (2)	12.206 (2)	16.349 (2)
α, deg	69.28 (1)		
β, deg	76.74 (1)	101.54 (1)	93.31 (1)
γ, deg	64.90 (1)		
vol, Å^3	1135.2 (3)	2580 (1)	3688 (1)
Z	2	4	8
ρ(calcd), g cm^{-3}	1.53	1.52	1.68
ρ(measd), g cm^{-3}	1.55	1.55	1.71
cryst dimen (dist, in mm from centroid)	±(100) 0.125 ±(101) 0.138 ±(010) 0.088 ±(001) 0.165	±($\bar{1}$20) 0.103 (120) 0.073 ($\bar{1}\bar{1}$0) 0.073 (100) 0.040 ±(001) 0.207	±(110) 0.124 ±(1$\bar{1}$0) 0.080 ±(001) 0.234 (1$\bar{1}$1) 0.160
temp, K	295 (1)		
radiation, Å	Mo Kα (graphite monochromator) λ = 0.71069		
intensity control reflecns	3 every 4500 s 12% decrease	3 every 1800 s 8% decrease	3 every 4000 s 3% decrease
F(000)	532	1208	1872
μ, cm^{-1}	16.70	16.05	20.51
	absorption corrections applied using SHELX-76		
transmission factors			
max.	0.7902	0.8388	0.7433
min.	0.6556	0.7304	0.5908
2θ limits	$2 \leq 2\theta \leq 55$	$2 \leq 2\theta' \leq 50$	$2 \leq 2\theta \leq 55$
instrument	Enraf Nonius CAD-4F diffractometer		
no. of reflecns	6511	6018	11074
measd no. uniq reflcns	5194	4522	4225
R_{amal}[a]	0.020	0.023	0.016
no. reflcns used in refinement ($1 \geq 2\sigma$)	40091	2313	3545
refinement	least squares; function minimized $\Sigma w\Delta^2$		
R[b]	0.029	0.052	0.021
R_w[b]	0.029	0.055	0.020
hkl range	$-1 \leq h \leq 12$ $-13 \leq k \leq 13$ $-17 \leq l \leq 17$	$-2 \leq h \leq 12$ $-1 \leq k \leq 23$ $-14 \leq l \leq 14$	$-22 \leq h \leq 22$ $-1 \leq k \leq 17$ $-21 \leq l \leq 21$

[a] See ref 14. [b] See ref 15.

measured against internal Me_4Si; tellurium-125 spectra were recorded at 31.4 MHz with an external ^7Li lock and referenced against external aqueous 0.7 M K_2TeO_3. Phosphorus-31 spectra were measured at 40.26 MHz and referenced against external 85% H_3PO_4. High frequency positive convention is used.

Crystal Structure Determination and Refinement. Crystals of each complex were initially investigated by means of oscillation and Weissenberg photographic methods. Intensity data for all three crystal structures were collected at 295 (1) K on an Enraf-Nonius CAD-4F diffractometer with Mo Kα (graphite monochromatized) radiation (λ 0.71067 Å). Accurate cell dimensions were obtained from the setting angles of 25 carefully centered reflections, by using a least-squares procedure. Intensity measurements were made with the ω:2θ scan method. Three reflections, monitored every 4500 for **1**, 1800 for **2**, 4000 for **3** seconds X-ray exposure time, indicated an approximate 12% (**1**), 8% (**2**), and 3% (**3**) decrease in intensity during the data collection. The data were corrected in accordance with these variations as well as for Lorentz, polarization, and absorption effects but not for extinction; absorption corrections were numerically evaluated by Gaussian integration to a precision of 0.5%.[12a,13] Crystal data for the three compounds are given in Table I.

Table II. Final Fractional Atomic Coordinates for $C_8H_8Te(Etdtc)_2$

	x	*y*	*z*
C(1)	0.5853 (4)	0.1228 (4)	0.3687 (3)
C(2)	0.7234 (4)	0.1663 (3)	0.3227 (2)
C(3)	0.8488 (4)	0.1177 (4)	0.3815 (3)
C(4)	0.9767 (4)	0.1546 (5)	0.3389 (3)
C(5)	0.9855 (5)	0.2384 (5)	0.2343 (3)
C(6)	0.8628 (4)	0.2887 (4)	0.1757 (3)
C(7)	0.7307 (4)	0.2541 (3)	0.2182 (3)
C(8)	0.5935 (4)	0.3150 (4)	0.1553 (3)
Te	0.43056 (3)	0.21450 (2)	0.24683 (2)
S(1)	0.61927 (11)	−0.00234 (19)	0.17116 (7)
S(2)	0.40903 (12)	−0.10622 (11)	0.35387 (8)
C(9)	0.5520 (4)	−0.1407 (4)	0.2557 (3)
N(1)	0.6220 (3)	−0.2728 (3)	0.2388 (2)
C(10)	0.5769 (5)	−0.3977 (4)	0.3052 (3)
C(11)	0.6727 (6)	−0.4912 (5)	0.3973 (4)
C(12)	0.7488 (5)	−0.3055 (4)	0.1553 (3)
C(13)	0.6892 (7)	−0.2805 (6)	0.0539 (4)
S(3)	0.29078 (12)	0.42722 (10)	0.33673 (7)
S(4)	0.21195 (12)	0.54461 (12)	0.11388 (7)
C(14)	0.2019 (4)	0.5748 (4)	0.2293 (3)
N(2)	0.1297 (3)	0.7073 (3)	0.2454 (2)
C(15)	0.0701 (5)	0.8427 (4)	0.1573 (3)
C(16)	0.1909 (6)	0.9116 (5)	0.1113 (4)
C(17)	0.1036 (5)	0.7309 (4)	0.3482 (3)
C(18)	−0.0487 (6)	0.7211 (5)	0.4066 (4)

Each structure was solved by normal Fourier methods. Details of the refinement procedure are given in Table I. A full-matrix least-squares refinement procedure[15] was used with anisotropic temperature factors assigned to all non-hydrogen atoms. For **1** and **3**, all hydrogen atoms were located from the difference maps, and their parameters were refined by using isotropic temperature factors. A weighting scheme of the form $w = (\sigma^2(F) + gF^2)^{-1}$ was used. The parameter *g* was varied during the course of the refinement, and, at convergence, an analysis of variance indicated that an appropriate weighting scheme had been used. The refinement of **1** converged with $R = 0.029$, $R_w = 0.029$, and $g = 0.0003$. The final difference map showed peaks whose heights were less than 0.56 e Å^{-3}. The refinement of **3** converged with $R = 0.021$, $R_w = 0.020$ and $g = 0.00006$. The final difference map showed peaks whose heights were less than 0.31 e Å^{-3}.

The structure of **2** was refined by using a similar procedure, the refinement converging with $R = 0.055$. At this stage the high temperature factors of the atoms of the ethyl groups of the dithiophosphate ligands, together with some anomalous bond lengths and angles, suggested that some of these atoms may be disordered. A full difference map with these ethyl groups removed showed broad peaks which could not be resolved, and so the structure analysis was continued without disorder of the ethyl groups. A difference map calculated at this stage showed a number of peaks associated with the ethyl groups which were suggestive of hydrogen atoms, but due to suspected disorder these were not included. Only the hydrogens associated with the *o*-xylene-α,α′-diyl ligand were included in the model, and these were constrained at their estimated geometrical positions. The refinement was continued with a weighting scheme $w = k(\sigma^2(F) + gF^2)$ where *k* and *g* were varied in the refinement procedure. The refinement converged with $k = 2.07$, $g = 0.0007$, $R = 0.052$ and $R_w = 0.055$. Analysis of variance showed that an appropriate weighting scheme was used. After the final refinement cycle, the greatest residual electron density peak was 0.6 e Å^{-3}.

Calculations were carried out with the programs SHELX-76,[13] ORTEP,[16] DISTAN,[17] and MEAN PLANE[18] on a VAX 11/780 computer. Scattering curves for H, C, N, O, and S were those collected by Sheldrick,[13] while that of Te was taken from ref 12b, this being corrected for the real and imaginary anomalous dispersion terms.[12c]

Results and Discussion

Description of the Structure of $C_8H_8Te(Etdtc)_2$ (1). Final fractional atomic coordinates are given in Table II, and relevant

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(12) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; (a) Vol. IV, p 55. (b) Vol. IV, p 99. (c) Vol. IV, p 149.

(13) Sheldrick, G. M. SHELX-76 *Program for Crystal Structure Determination*; University of Cambridge: Cambridge, U.K., 1976.

(14) $R_{amal} = [\Sigma(N\Sigma(w(F_{mean} - F)^2))/\Sigma((N-1)\Sigma(wF^2))]^{1/2}$ where the inner summations are over *N* equivalent reflections averaged to give F_{mean}, the outer summations are over all unique reflections, and the weight, *w*, is taken as $(\sigma(F))^{1/2}$.

(15) The function minimized was $\Sigma w(|F_o| - |F_c|)^2$. The unweighted and weighted residuals were defined as $R = (\Sigma|F_o| - |F_c|)/\Sigma|F_o|$ and $R_w = \Sigma w^{1/2}(|F_o| - |F_c|)/\Sigma w^{1/2}|F_o|$.

(16) Johnson, C. K. "ORTEP"; Report ORNL-3794; Oak Ridge National Laboratory; Oak Ridge, TN, 1965.

(17) Kelly, B. P.; O'Day, B. P.; Pannan, C. D. University of Melbourne, 1974.

(18) Ahmed, F. R.; Pippy, M. E. Division of Pure Physics, National Research Council, Ottawa, Canada 1967.

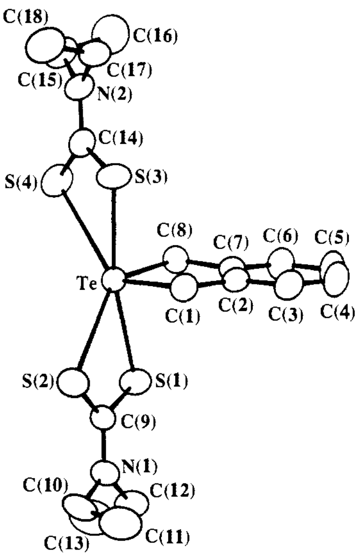

Figure 1. ORTEP of 1,3-dihydro-2λ^4-benzotellurole-2,2-diyl bis(diethyldithiocarbamate), $C_8H_8Te(Etdtc)_2$, **1**.

Table III. Final Fractional Atomic Coordinates for $C_8H_8Te(Etdtp)_2$

	x	*y*	*z*
Te	0.03996 (7)	0.26413 (4)	0.47764 (5)
C(1)	0.1029 (12)	0.3447 (5)	0.3873 (8)
C(2)	0.1968 (10)	0.3829 (5)	0.4658 (9)
C(3)	0.2484 (13)	0.4396 (6)	0.4294 (12)
C(4)	0.3379 (14)	0.4733 (8)	0.5025 (15)
C(5)	0.3814 (15)	0.4511 (9)	0.6120 (14)
C(6)	0.3323 (13)	0.3937 (7)	0.6500 (11)
C(7)	0.2368 (11)	0.3594 (5)	0.5756 (8)
C(8)	0.1745 (10)	0.2988 (5)	0.6152 (7)
S(1)	−0.1131 (4)	0.3573 (2)	0.5246 (3)
S(2)	−0.1309 (3)	0.2213 (2)	0.6815 (3)
P(1)	−0.2119 (4)	0.3006 (2)	0.6160 (3)
O(1)	−0.2689 (17)	0.3480 (7)	0.6890 (15)
O(2)	−0.3464 (12)	0.2764 (8)	0.5305 (13)
C(9)	−0.2120 (30)	0.3728 (11)	0.7876 (24)
C(10)	−0.2768 (23)	0.4102 (10)	0.8506 (17)
C(11)	−0.4303 (27)	0.3134 (12)	0.4603 (21)
C(12)	−0.4869 (23)	0.2897 (16)	0.3641 (22)
S(3)	0.2247 (3)	0.2011 (2)	0.4123 (2)
S(4)	0.1202 (5)	0.1098 (2)	0.6000 (3)
P(2)	0.2251 (4)	0.1121 (2)	0.4924 (3)
O(3)	0.2016 (12)	0.0555 (6)	0.4006 (10)
O(4)	0.3702 (14)	0.0934 (7)	0.5368 (15)
C(13)	0.0953 (17)	0.0366 (11)	0.3368 (17)
C(14)	0.1000 (15)	−0.0094 (7)	0.2455 (11)
C(15)	0.4536 (33)	0.1167 (18)	0.6027 (28)
C(16)	0.5664 (20)	0.0813 (11)	0.6326 (18)

Table IV. Final Fractional Atomic Coordinates for $C_8H_8Te(Etxan)_2$

	x	*y*	*z*
C(1)	0.2131 (1)	−0.1052 (1)	0.2008 (1)
C(2)	0.2382 (1)	−0.1110 (1)	0.1163 (1)
C(3)	0.3113 (1)	−0.1502 (2)	0.1064 (2)
C(4)	0.3331 (1)	−0.1572 (2)	0.0284 (2)
C(5)	0.2827 (2)	−0.1258 (2)	−0.0398 (2)
C(6)	0.2098 (1)	−0.0983 (2)	−0.0306 (1)
C(7)	0.1873 (1)	−0.0794 (1)	0.0475 (1)
C(8)	0.1078 (1)	−0.0377 (2)	0.0564 (1)
Te	0.06434 (4)	−0.24172 (5)	0.15561 (4)
S(2)	−0.08721 (4)	−0.12917 (5)	0.11497 (4)
C(9)	−0.0367 (1)	−0.2345 (2)	0.1303 (1)
O(1)	−0.0673 (1)	−0.3264 (1)	0.1254 (1)
C(10)	−0.1533 (2)	−0.3401 (3)	0.1065 (3)
C(11)	−0.1756 (3)	−0.3526 (4)	0.0165 (4)
S(3)	0.16359 (3)	0.12626 (4)	0.20903 (4)
S(4)	−0.00422 (3)	0.15620 (5)	0.13219 (4)
C(12)	0.0830 (1)	0.1989 (2)	0.1718 (1)
O(2)	0.1011 (1)	0.2967 (1)	0.1811 (1)
C(13)	0.0423 (2)	0.3706 (2)	0.1486 (3)
C(14)	0.0778 (3)	0.4712 (3)	0.1712 (4)

Table V. Significant Bond Lengths (Å) and Angles (deg) for $C_8H_8Te(Etdtc)_2$

atoms	distance	atoms	distance
Te–C(1)	2.150 (4)	N(1)–C(10)	1.470 (5)
Te–C(8)	2.143 (4)	N(1)–C(12)	1.467 (5)
Te–S(1)	2.599 (1)	C(12)–C(13)	1.509 (7)
Te–S(2)	3.220 (1)	C(10)–C(11)	1.502 (7)
Te–S(3)	2.622 (1)	S(3)–C(14)	1.760 (4)
Te–S(4)	3.270 (1)	S(4)–C(14)	1.687 (4)
C(1)···C(8)	2.899 (5)	C(14)–N(2)	1.332 (5)
S(1)···S(2)	2.997 (2)	N(2)–C(15)	1.481 (5)
S(3)···S(4)	2.988 (1)	C(15)–C(16)	1.505 (8)
S(1)–C(9)	1.756 (4)	N(2)–C(17)	1.457 (5)
S(2)–C(9)	1.688 (4)	C(17)–C(18)	1.503 (8)
C(9)–N(1)	1.332 (5)		

atoms	angle	atoms	angle
C(1)–Te–C(8)	84.9 (2)	S(2)–C(9)–N(1)	122.8 (3)
C(1)–Te–S(1)	87.1 (2)	C(9)–N(1)–C(10)	121.2 (3)
C(1)–Te–S(2)	79.3 (1)	C(9)–N(1)–C(12)	123.4 (3)
C(1)–Te–S(3)	82.9 (1)	C(10)–N(1)–C(12)	115.3 (3)
C(1)–Te–S(4)	136.7 (1)	N(1)–C(10)–C(11)	113.3 (4)
C(8)–Te–S(1)	82.6 (1)	N(1)–C(12)–C(13)	112.7 (4)
C(8)–Te–S(2)	140.6 (1)	Te–S(3)–C(14)	100.0 (4)
C(8)–Te–S(3)	90.9 (1)	Te–S(4)–C(14)	79.8 (1)
C(8)–Te–S(4)	75.2 (1)	S(3)–C(14)–S(4)	120.2 (2)
S(1)–Te–S(2)	60.89 (3)	S(3)–C(14)–N(2)	116.2 (3)
S(1)–Te–S(3)	168.55 (4)	S(4)–C(14)–N(2)	123.6 (3)
S(1)–Te–S(4)	126.73 (3)	C(14)–N(2)–C(15)	121.1 (3)
S(2)–Te–S(3)	122.18 (3)	C(14)–N(2)–C(17)	123.6 (3)
S(3)–Te–S(4)	59.74 (3)	N(2)–C(15)–C(16)	110.7 (4)
Te–S(1)–C(9)	98.7 (1)	N(2)–C(17)–C(18)	111.9 (4)
Te–S(2)–C(9)	79.4 (1)	C(15)–N(2)–C(17)	115.3 (3)
S(1)–C(9)–S(2)	121.0 (2)	Te–C(1)–C(2)	107.2 (2)
S(1)–C(9)–N(1)	116.3 (3)	Te–C(8)–C(7)	107.3 (3)

bond lengths and angles are listed in Table V. An ORTEP diagram of the molecule showing the numbering scheme is shown in Figure 1. The C_8H_8 group is symmetrically bonded to the tellurium(IV) atom, with the two tellurium–carbon bond lengths of 2.143 (4) and 2.150 (4) Å being similar to those found for $C_8H_8TeI_2$.[20] The coordination geometry formed by the four closest atoms C(1), C(8), S(1), and S(3) is approximately trigonal bipyramidal, with the sulfur atoms in the apical positions [Te–S(1) 2.599 (1), Te–S(3) 2.622 (1) Å] and the two carbon atoms in the equatorial plane [C(1)–Te–C(8) 84.9 (2)°]. The fifth coordination position, in the equatorial plane, is apparently occupied by a sterically active lone pair. The S(1)–Te–S(3) angle of 168.55 (4)° deviates considerably from linearity with both sulfur atoms pushed away from the equatorial tellurium lone pair. The two remaining sulfur atoms form somewhat longer bonds to tellurium [Te–S(2) 3.220 (1), Te–S(4) 3.270 (1) Å] which are still well within the sum of the respective van der Waals radii of 3.86 Å.[19]

These longer tellurium–sulfur bonds, Te–S(2) and Te–S(4), are situated through two of the faces of the trigonal bipyramid, bounded by C(1), S(1) and the lone electron pair for S(2) and C(8), S(3) and the lone electron pair for S(4). Thus the tellurium atom has an effective coordination number of seven and has close to a 1:2:2:2 geometry.[21] The dihedral angle between the two dithiocarbamate ligands is 120°. The tellurium atom is almost coplanar with the carbon atoms of the C_8H_8 group. It is also notable that the molecule has an approximate 2-fold axis along the tellurium–lone pair direction, although no crystallographic 2-fold axis is present.

Description of the Structure of $C_8H_8Te(Etdtp)_2$ (2). Final fractional atomic coordinates are given in Table III, and relevant

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Table VI. Significant Bond Distances (Å) in $C_8H_8Te(Etdtp)_2$

atoms	distance	atoms	distance	atoms	distance
Te–C(1)	2.133 (11)	Te–C(8)	2.109 (9)	Te–S(1)	2.627 (4)
Te–S(2)	3.493 (4)	Te–S(3)	2.621 (3)	Te–S(4)	3.447 (4)
Te–S(2^{1})^{a}	3.729 (4)	C(1)–C(2)	1.464 (15)	C(2)–C(3)	1.371 (16)
C(2)–C(7)	1.404 (14)	C(3)–C(4)	1.357 (21)	C(4)–C(5)	1.397 (24)
C(5)–C(6)	1.378 (22)	C(6)–C(7)	1.410 (17)	C(7)–C(8)	1.508 (14)
S(1)–P(1)	2.036 (6)	S(2)–P(1)	1.901 (6)	P(1)–O(1)	1.512 (17)
P(1)–O(2)	1.686 (15)	O(1)–C(9)	1.333 (33)	O(2)–C(11)	1.339 (30)
C(9)–C(10)	1.362 (36)	C(11)–C(12)	1.300 (37)	S(3)–P(2)	2.021 (5)
S(4)–P(2)	1.903 (6)	P(2)–O(3)	1.572 (13)	P(2)–O(4)	1.604 (16)
O(3)–C(13)	1.311 (23)	O(4)–C(15)	1.179 (38)	C(13)–C(14)	1.450 (25)
C(15)–C(16)	1.396 (41)				

$^{a\,1}x,\ {}^{1}/_{2} - y,\ -{}^{1}/_{2} + z.$

Table VII. Significant Bond Angles (deg) in $C_8H_8Te(Etdtp)_2$

atoms	angle	atoms	angle
C(8)–Te–S(2^{1})^{a}	151.3 (3)	Te–C(1)–C(2)	107.7 (7)
Te–S(1)–P(1)	98.9 (2)	Te–S(2)–P(1)	76.4 (2)
Te–C(8)–C(7)	106.8 (6)	C(1)–C(2)–C(7)	119.6 (9)
C(1)–C(2)–C(3)	119 (1)	C(2)–C(3)–C(4)	119 (1)
C(3)–C(4)–C(5)	122 (1)	C(4)–C(5)–C(6)	120 (1)
C(5)–C(6)–C(7)	118 (1)	C(6)–C(7)–C(2)	120 (1)
C(6)–C(7)–C(8)	120 (1)	S(1)–P(1)–S(2)	116.1 (3)
S(1)–Te–S(3)	163.6 (1)	S(1)–Te–S(4)	130.5 (1)
S(1)–Te–C(8)	87.9 (3)	S(1)–Te–C(1)	82.3 (3)
S(2)–Te–S(3)	130.4 (1)	S(2)–Te–S(4)	66.3 (1)
S(1)–Te–S(2)	64.35 (11)	S(2)–Te–C(8)	83.9 (3)
S(2)–Te–C(1)	145.3 (3)	C(1)–Te–C(8)	85.6 (4)
O(1)–P(1)–S(1)	107.5 (6)	O(1)–P(1)–S(2)	118.6 (7)
O(2)–P(1)–S(2)	107.1 (6)	O(2)–P(1)–S(1)	107.7 (6)
O(2)–P(1)–O(1)	97.9 (9)	C(9)–O(1)–P(1)	126 (2)
C(10)–C(9)–O(1)	121 (3)	C(11)–O(2)–P(1)	129 (2)
C(12)–C(11)–O(2)	121 (2)	S(3)–P(2)–S(4)	114.3 (3)
S(3)–Te–S(4)	64.13 (11)	S(3)–Te–C(8)	87.0 (3)
S(3)–Te–C(1)	81.8 (3)	S(4)–Te–C(8)	82.6 (3)
S(4)–Te–C(1)	144.4 (3)	P(2)–S(3)–Te	101.5 (2)
P(2)–S(4)–Te	79.3 (2)	P(2)–O(4)–C(15)	135 (2)
O(3)–P(2)–O(4)	94.8 (8)	O(3)–P(2)–S(3)	107.3 (5)
O(3)–P(2)–S(4)	116.1 (5)	O(4)–C(15)–C(16)	120 (3)
O(4)–P(2)–S(4)	116.4 (7)	O(4)–P(2)–S(3)	105.9 (6)
C(14)–C(13)–O(3)	118 (2)	C(13)–O(3)–P(2)	129 (1)

$^{a\,1}x,\ {}^{1}/_{2} - y,\ -{}^{1}/_{2} + z.$

bond lengths and angles are given in Tables VI and VII. The ORTEP diagram is shown in Figure 2. The coordination geometry formed by the four atoms closest to the tellurium(IV) atom, C(1), C(8), S(1), S(3), is approximately trigonal bipyramidal, with the sulfur atoms in the apical positions [Te–S(1) 2.627 (4), Te–S(3) 2.621 (3) Å; S(1)–Te–S(3) 163.6 (1)°] and two carbons in the equatorial plane [Te–C(1) 2.133 (11), Te–C(8) 2.109 (9) Å; C(1)–Te–C(8) 85.6 (4)°]. The fifth coordination position, in the equatorial plane, is apparently occupied by a sterically active lone pair. The S(1)–Te–S(3) angle of 163.6 (1)° deviates considerably from linearity with both sulfur atoms pushed away from the equatorial lone electron pair. In addition there are three further sulfur atoms S(2), S(4), and S(2^{1}) (where I refers to that atom related by the symmetry operation $x, {}^{1}/_{2} - y, -{}^{1}/_{2} + z$) which form secondary interactions with the tellurium atom and which are all shorter than the sum of the van der Waals radii of 3.86 Å.[19]

Two of these interactions [Te–S(2) 3.493 (4), Te–S(4) 3.447 (4) Å] are intramolecular and are arranged such that the atoms S(1), S(2), S(3), S(4), and C(1) form a pentagonal plane about the tellurium which lies 0.2 Å out of this plane. The third secondary interaction to the tellurium atom, [Te–S(2^{1}) 3.729 (4) Å] which is below the pentagonal plane [C(8)–Te–S(2^{1}) 151.3 (3)°] is the basis of a zigzag polymer chain. The spatial arrangement of the dithiophosphate ligands relative to the tellurium atom results in a planar four-membered ring in one case and a slightly puckered ring in the other. The two four-atom planes are almost coplanar being at 1.5° to each other. The *o*-xylene-*α*,*α*′-diyl group (C_8H_8) is planar and is at 89.6° to the pentagonal plane.

Inclusion of the secondary interactions gives an effective eight coordination about the tellurium atom. According to the VSEPR theory,[32] the eight electron pairs should be arranged at the corners of a dodecahedron or a square antiprism. The actual geometry appears to be that of an irregular dodecahedron with distortions probably arising from restrictions imposed by the two four-

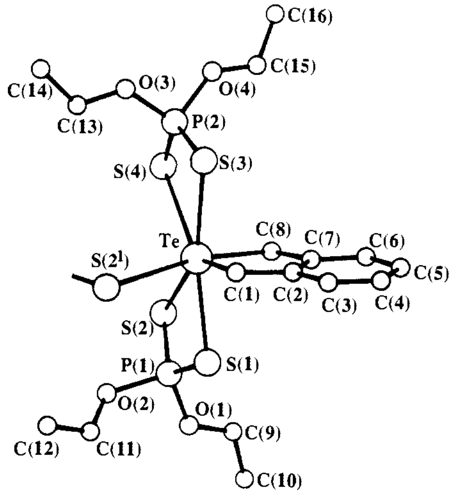


Figure 2. ORTEP of *S*,*S*′-(1,3-dihydro-2λ^{4}-benzotellurole-2,2-diyl) *O*,*O*,*O*′,*O*′-tetraethyl bis(dithiophosphate), $C_8H_8Te(Etdtp)_2$, **2**.

Table VIII. Significant Bond lengths (Å) and angles (°) for $C_8H_8Te(Etxan)_2$.

atoms	distance	atoms	distance
Te–C(1)	2.125 (2)	C(9)–O(1)	1.327 (3)
Te–C(8)	2.143 (2)	O(1)–C(10)	1.475 (4)
Te–S(1)	2.6142 (7)	C(10)–C(11)	1.475 (8)
Te–S(2)	3.3220 (7)	S(3)–C(12)	1.724 (2)
Te–S(3)	2.6410 (5)	S(4)–C(12)	1.644 (2)
Te–S(4)	3.2720 (6)	C(12)–O(2)	1.338 (3)
Te–S(2^{1})^{a}	3.4796 (7)	O(2)–C(13)	1.452 (4)
S(1)–C(9)	1.727 (2)	C(13)–C(14)	1.493 (5)
S(2)–C(9)	1.646 (3)		
atoms	**angle**	**atoms**	**angle**
C(1)–Te–C(8)	85.60 (7)	S(3)–Te–S(2^{1})^{a}	101.03 (2)
C(1)–Te–S(1)	81.70 (7)	S(4)–Te–S(2^{1})^{a}	113.91 (2)
C(1)–Te–S(2)	140.13 (7)	Te–S(1)–C(9)	98.83 (9)
C(1)–Te–S(3)	83.19 (7)	Te–S(2)–C(9)	76.55 (7)
C(1)–Te–S(4)	139.87 (7)	S(1)–C(9)–S(2)	124.9 (2)
C(1)–Te–S(2^{1})^{a}	86.25 (5)	S(1)–C(9)–O(1)	109.8 (2)
C(8)–Te–S(1)	87.57 (7)	S(2)–C(9)–O(1)	125.3 (1)
C(8)–Te–S(2)	85.83 (5)	C(9)–O(1)–C(10)	120.1 (2)
C(8)–Te–S(3)	88.49 (7)	O(1)–C(10)–C(11)	109.3 (3)
C(8)–Te–S(4)	78.94 (7)	Te–S(3)–C(12)	97.01 (8)
C(8)–Te–S(2^{1})^{a}	166.65 (7)	Te–S(4)–C(12)	77.38 (9)
S(1)–Te–S(2)	59.08 (2)	S(3)–C(12)–S(4)	125.8 (2)
S(1)–Te–S(3)	164.63 (2)	S(3)–C(12)–O(2)	110.0 (1)
S(1)–Te–S(4)	133.59 (2)	S(4)–C(12)–O(2)	124.2 (2)
S(1)–Te–S(2^{1})^{a}	80.80 (2)	C(12)–O(2)–C(13)	118.5 (2)
S(2)–Te–S(3)	135.36 (2)	O(2)–C(13)–C(14)	106.1 (3)
S(2)–Te–S(4)	75.66 (2)	Te–C(1)–C(2)	106.6 (1)
S(2)–Te–S(2^{1})^{a}	93.70 (2)	Te–C(8)–C(7)	107.1 (1)
S(3)–Te–S(4)	59.80 (2)		

$^{a\,1}-x,\ y,\ {}^{1}/_{2} - z.$

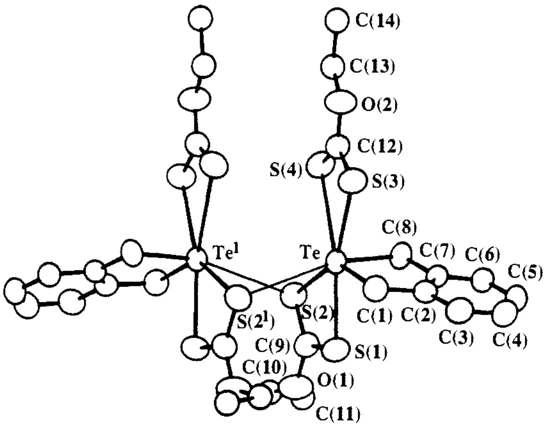


Figure 3. ORTEP of (1,3-dihydro-2λ^4-benzotellurole-2,2-diyl) bis(*O*-ethyl xanthate), $C_8H_8Te(Etxan)_2$, **3**.

membered (TeS_2P) rings and the five-membered (TeC_4) ring.

Description of the Structure of $C_8H_8Te(Etxan)_2$ (3). Final fractional atomic coordinates are given in Table IV, and relevant bond lengths and angles are listed in Table VIII. An ORTEP diagram of the molecule is shown in Figure 3. The tellurium(IV) atom is bonded to the two methylene carbon atoms of the C_8H_8 group and two anisobidentate xanthate ligands. The four closest donor atoms, C(1), C(8), S(1), and S(3), provide a trigonal bipyramidal primary coordination environment about the tellurium atom, with the two sulfur atoms occupying apical positions [Te–S(1) 2.614 (1), Te–S(3) 2.641 (1) Å; S(1)–Te–S(3) 164.63 (1)°] and the two carbon atoms and the tellurium lone pair forming the equatorial plane [Te–S(1) 2.125 (2), Te–C(8) 2.143 (2) Å; C(1)–Te–C(8) 85.60 (7)°]. In addition there are three further sulfur atoms S(2), S(4), and S(2^1) (where I refers to that atom related by the symmetry operation $-x$, y, $^1/_2 - z$) which coordinate to the tellurium atom forming somewhat longer secondary interactions which are all smaller than the sum of the van der Waals radii of 3.86 Å.[19] Two of these interactions, Te–S(4) and Te–S(2) [3.272 (1), 3.322 (1) Å, respectively], are intramolecular and take place such that S(1), S(2), S(3), S(4), and C(1) form a pentagonal plane about the tellurium atom. The third secondary interaction to the tellurium atom is with S(2^1)[Te–S(2^1) 3.480 (1) Å] which results in a dimeric association around a 2-fold axis. The C(8)–Te–S(2^1) angle is 166.65 (7)°.

There are no other atom contacts less than the sum of the van der Waals radii of the atoms involved. Although the structure appears to be a distorted pentagonal bipyramid, the fact that atom S(2^1) is displaced away from the axial position implies that the lone electron pair is stereochemically active. To support this, the atoms adjacent to the region thought to be occupied by the lone pair are found to have longer bonds to the tellurium atom [i.e., Te–S(2) 3.322 (1); Te–S(4) 3.272 (1); Te–S (2^1) 3.480 (1) Å]. The tellurium center is thus effectively eight coordinate, with a geometry best described as intermediate between a dodecahedron and an interpenetrating pentagon geometry.

Comparison of Structures 1, 2, and 3. One major difference between the three compounds is noticeable in the Te–S(2) and Te–S(4) distances. These bonds are found to be slightly shorter in the dithiocarbamate complexes than in the xanthate complex, presumably due to a stronger chelating ability of the dithiocarbamate ligand. The longest tellurium–sulfur bonds are found in the dithiophosphate complex which may result from the larger "bite"[33] of the dithiophosphate chelate, as reflected in the S(1)–Te–S(2), S(3)–Te–S(4) angles. A more important difference is the effective coordination number of the tellurium in each of the three complexes. Since **2** and **3** have similar bond lengths, angles, and a coordination number of eight (including the lone pair of electrons), they adopt approximately the same stereochemistry. On the other hand, complex **1** has a coordination number of seven (including the lone pair of electrons) and adopts a different stereochemistry. Presumably, the lower coordination number reflects the stronger donor capabilities of the dithiocarbamate ligand, as compared with dithiophosphates and xanthates. It is also noteable that in all three structures, the longer Te–S(2), Te–S(4) bonds are clustered about the region associated with the position of the tellurium lone electron pair. Similar directional effects of the lone electron pair have been observed for a number of other tellurium(IV) compounds,[3,24–26,34–38] and it seems reasonable to suppose that these observations are a consequence of the tellurium(IV) atom to increase its coordination number rather than crystal packing forces.

Table IX. Tellurium-125 and Carbon-13 Chemical Shifts (ppm) for Compounds **1**, **2**, and **3** at 30 °C

(a) Tellurium-125 Shifts

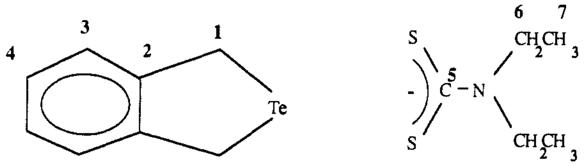
	solvent				
compd	dcm	thf	diox	py	dmf
1	−1121	−1119	−1115	−1113	−1119
2	−999	−990	−986	−952	−952
3	−1066	−1052	−1046	−1021	−1022

(b) Carbon-13 Shifts[a] (in Dichloromethane Solution)

	carbon number						
compd	1	2	3	4	5	6	7
1	44.6	140.7	127.6	130.6	199.2	48.9	12.4
2	44.7	139.0	127.9	130.0		63.6[c]	15.8[c]
3	44.7	140.2	128.3	130.7	221.6	71.5	14.4

[a] Carbon atom assignments given in Chart I. [b] Split into two resonances 11.3, 12.2 ppm at −90 °C. [c] $^2J_{c-p} = {}^3J_{c-p} = 7$ Hz.

Chart I



Infrared Spectroscopy. The infrared spectra of **1** as a KBr disc and in CS_2 solution are almost identical. There are very slight differences in the γ_{CS} band at 984.6 cm^{-1} which are consistent with, but not proof for, monodentate dithiocarbamate groups in solution which become closer to bidentate in the solid state.[27] The infrared spectra of **3** are also very similar for the solid and in CS_2 solution with both spectra having bands at 1043.2 and 1031.7 cm^{-1}, attributed to γ_{CS} vibrations.[28] There are more pronounced differences in the γ_{CO} region where the band at 1197.9 cm^{-1} is symmetric in CS_2 solution and asymmetric in the solid state at 1189.8 cm^{-1}. These observations are consistent with monodentate behavior of the xanthate in solution. The infrared spectra of **2** as a KBr disc and in CS_2 solution are almost identical and do not yield any substantive information about the nature of coordination of the dithiophosphate ligand.

NMR Spectroscopy on 1, 2, and 3. Of the three structures, only **1** is strictly monomeric in the solid state, whereas the structures of **2** and **3** both show additional interactions with adjacent

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Table X. Tellurium-125 and Phosphorus-31 Data for Various Tellurium(IV) Dithiolate Complexes in Dichloromethane Solution at 30 °C

species	δ (^{125}Te)	δ (^{31}P)	species	δ (^{125}Te)	δ (^{31}P)
$C_8H_8Te(^iPrdtc)_2$	−1142		$C_8H_8Te(Etdtc)(^iPrdtp)$	−1055[b]	97.6
$C_8H_8Te(^iPrdtp)_2$	−1018	93.1	$C_8H_8Te(^iPrdtc)(Etdtp)$	−1072[c]	101.4 brd
$C_8H_8Te(^iPrxan)_2$	−1058		$C_8H_8Te(^iPrdtc)(^iPrdtp)$[d]	−1062	
$C_8H_8Te(Etdtc)(Etxan)$	−1098		$C_8H_8Te(Etdtc)(^iPrdtc)$	−1131	
$C_8H_8Te(Etdtp)(Etxan)$	−1038		$C_8H_8Te(Etdtp)(^iPrdtp)$	−1008	92.1, 95.1
$C_8H_8Te(Etdtc)(Etdtp)$	−1060[a]	99.3	$C_8H_8Et(Etxan)(^iPrxan)$	−1062	

[a] Doublet at −60 °C $J_{(Te-P)} = 29$ Hz. [b] Doublet at −60 °C $J_{Te-P} = 27$ Hz. [c] Two doublets −1069, −1090 ppm $J_{Te-P} = 27$ Hz; δ (^{31}P) 100.1, 100.3 at −90 °C. [d] In chloroform solution.

molecules. This structural difference is also reflected in the tellurium-125 chemical shifts of the three compounds in different solvents at 30 °C (Table IX). The changes in ^{125}Te shifts which occur when **2** and **3** are dissolved in strong donor solvents imply that they undergo significant interactions with these solvents. On the other hand, the ^{125}Te shift of **1** is relatively unaffected by the nature of the solvent which implies that **1** is coordinately saturated and does not interact with the strong donor solvents used. This trend in ^{125}Te shifts reflects the stronger donor ability of dithiocarbamate compared with dithiophosphate and xanthate ligands.

In order to assess the rate of intermolecular dithiolate ligand exchange the isopropyl analogue to **1**, **2**, and **3** was synthesized and investigated. The ^{125}Te spectrum of an equimolar mixture $C_8H_8Te(Etdtc)_2$ and $C_8H_8(^iPrdtc)_2$ in dichloromethane solution at 30 °C shows three resonances [δ(^{125}Te) −1121, −1131, −1142 ppm] of relative intensities 1:2:1. The outer two resonances are at chemical shift positions for $C_8H_8Te(Etdtc)_2$ and $C_8H_8Te(^iPrdtc)_2$, respectively, whilst the central, most intense resonance, δ(^{125}Te) −1131 ppm, is assigned to the mixed-ligand species $C_8H_8Te(Etdtc)(^iPrdtc)$, formed according to the redistribution scheme.

$$C_8H_8Te(Etdtc)_2 + C_8H_8Te(^iPrdtc)_2 \rightleftharpoons 2C_8H_8Te(Etdtc)(^iPrdtc)$$

Similarly, ^{125}Te spectra indicative of the redistribution reaction are observed at 30 °C for solutions containing equimolar mixtures of $C_8H_8Te(Etdtp)_2/C_8H_8Te(^iPrdtp)_2$ and $C_8H_8Te(Etxan)_2/C_8H_8Te(^iPrxan)_2$ (Table X). The simultaneous observation of all three possible species in these mixed-ligand experiments demonstrates that whilst dithiolate exchange is rapid on the preparative time scale, it is slow on the NMR time scale.

At room temperature the ^{13}C resonances of each of the three compounds **1**, **2**, and **3** show that the two dithiolate ligands are equivalent as are the methylene carbons adjacent to tellurium (Table IX). This observed equivalence of the two dithiolate ligands within each of **1**, **2**, and **3** may result from the fact that the structures in solution are similar to those in the solid but with the dithiolate ligands undergoing rapid intramolecular monodentate–bidentate exchange. Alternatively, equivalence would also occur if the dithiolate chelates undergo rapid intermolecular exchange at room temperature, but this possibility was eliminated by the above mixed-ligand experiments. At temperatures as low as −110 °C, in dichloromethane solution, the ^{13}C resonances for **2** and **3** are broadened but otherwise show no significant changes from the room temperature spectra. However the ^{13}C spectrum for **1** at −90 °C displays two resonances for the methyl carbon atoms of the dithiocarbamate ligands. One interpretation of this could be that the two dithiocarbamate ligands are in different environments but this is unlikely as only one dithio (i.e., S_2C-) ^{13}C resonance is observed. Furthermore, for the complex $C_8H_8TeI(Etdtc)$, where only one dithiocarbamate ligand is present, similar spectral changes were observed for the methyl ^{13}C resonances at low temperature.[39] Therefore the implication is that the two ethyl groups within each dithiocarbamate ligand are in different environments. Alternatively, the variable-temperature ^{13}C spectra of **1** may be accounted for by invoking a rapid intramolecular monodentate–bidentate ligand exchange at room temperature which slows at low temperature such that the dithiocarbamate ligand remains bidentate, and the structure in solution (Figure 4) approximates that observed in the solid state. Even when monodentate–bidentate exchange is slow in solution at low temperature, it is likely that the molecule still possesses appreciable internal vibrational energy. The effect of this vibrational energy is to make the Te–S distances equivalent (i.e., to make the ligands isobidentically chelated to the tellurium atom) albeit somewhat longer than those observed in the solid state.

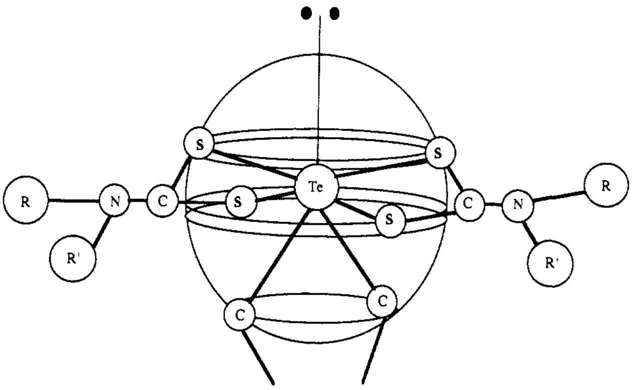

Figure 4. The 1:2:2:2 geometry proposed for **1** in solution at low temperature.

In the 1:2:2:2 structure shown in Figure 4, each dithiocarbamate ligand is isobidentically chelated to the tellurium atom through the four sulfur atoms of the two dithiocarbamate ligands. Two sulfurs, one from each dithiocarbamate ligand, are closer to the C_8H_8 portion of the molecule, and the remaining two sulfurs are closer to the lone pair of electrons. In this configuration the two ethyl groups of each dithiocarbamate ligand become nonequivalent (i.e., anisochronous) thus explaining the spectral changes observed at low temperatures in the ethyl region of the ^{13}C spectrum. However, the above NMR data are also consistent with a six-coordinate cis octahedral geometry in which the lone electron pair is stereochemically inert. Although the NMR data cannot distinguish between the two geometries, it seems reasonable to assume that, since the lone electron pair is obviously stereochemically active in the solid-state structure and since the ligands remain chelated to the tellurium atom in solution, the lone electron pair is also stereochemically active in solution at low temperatures.

NMR Spectroscopy of $C_8H_8Te(^iPrdtc)_2$. The compound $C_8H_8Te(^iPrdtc)_2$ was studied in more detail to test the possibility that the bulkier isopropyl group might slow intramolecular exchange processes at higher temperatures than found for the ethyl analogue **1**. The ^{125}Te spectrum of $C_8H_8Te(^iPrdtc)_2$ in dichloromethane solution at −40 °C consists of a single resonance which is broadened ($w_{1/2} = 120$ Hz) but not significantly shifted from the room temperature position. At −80 °C, the ^{125}Te spectrum comprises three broad resonances [δ(^{125}Te) −1148, −1166, −1187 ppm; $w_{1/2} \approx 120$ Hz]. When the temperature is

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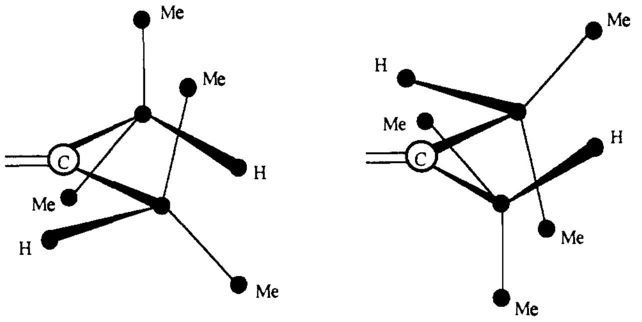

Figure 5. The two possible conformers of geminal isopropyl groups in isopropylethylenes.

lowered to −90 °C, the three signals sharpen, and their approximate intensities are 1.0:2.8:1.6.

The methine ^{13}C resonances of the dithiocarbamate ligand are obscured by the dichloromethane; however, in chloroform solution the methine resonance is observed but is very broad and split [$\delta(^{13}C)$ 52.3, 55.5 ppm]. A single ^{13}C resonance is observed for the two methylene carbons adjacent to tellurium. Three ^{13}C resonances are observed for the aromatic carbons, indicating that the C_8H_8Te portion of the molecule lies on an axis of symmetry. The two diisopropyldithiocarbamate ligands give only one resonance for the dithio carbons (i.e., S_2C-), and also one resonance only is observed for the two methyl groups (Table XI).

The ^{13}C resonances are all sharp at −40 °C, and only one dithio ^{13}C resonance (i.e., S_2C-) is observed as well as only one signal for the methylene carbons adjacent to tellurium. The three aromatic ^{13}C resonances are unchanged from the room temperature spectrum. The resonance due to the methyl groups is split into two signals [$\delta(^{13}C)$ 19.6, 20.2 ppm] indicating that the methyl groups within the same dithiocarbamate ligand are now in different chemical environments (i.e., anisochronous). The methine ^{13}C resonances are now well separated [$\delta(^{13}C)$ 57.3, 50.8 ppm] showing that they, even more so than the methyl groups, reflect the different chemical environments.

The ^{13}C spectrum recorded at −90 °C in dichloromethane solution (at this temperature none of the ^{13}C resonances are obscured by the solvent resonance) shows two dithio (i.e., S_2C−) carbon resonances [$\delta(^{13}C)$ 196.1, 194.5 ppm] indicating that two different types of dithiocarbamate ligand are present at this temperature. The methyl carbon atoms show a broad unresolved multiplet at $\delta(^{13}C)$ 17.0 ppm, whilst the methine ^{13}C resonance now comprises two sets of doublets [$\delta(^{13}C)$ 56.0, 54.7, 49.3, 48.3 ppm].

In order to understand the above spectral changes, it is useful first to describe some general structural effects of isopropyl groups. Geminal isopropyl groups attached to a planar framework generally adopt conformations in which the methine hydrogen of one group is tucked into the cleft formed by the two methyls of the neighboring group.[40–45] A recent report of an investigation by dynamic proton NMR of the barrier to rotation in isopropylethylenes indicates that conversion of one conformer to another (Figure 5) is slow on the NMR time scale at −65 °C and results in two sets of proton resonances of equal intensities.[46] The barrier to rotation at −65 °C is reasonably high at 42.6 kJ mol^{-1}. An examination of crystal structures of some complexes containing diisopropyldithiocarbamates[43,44,46–50] shows that in complexes containing anisobidentate dithiocarbamates, the methine hydrogen of one isopropyl group lies between the two methyls of the adjacent isopropyl group, and the other methine hydrogen always points to the sulfur atom which has the longer metal interaction.

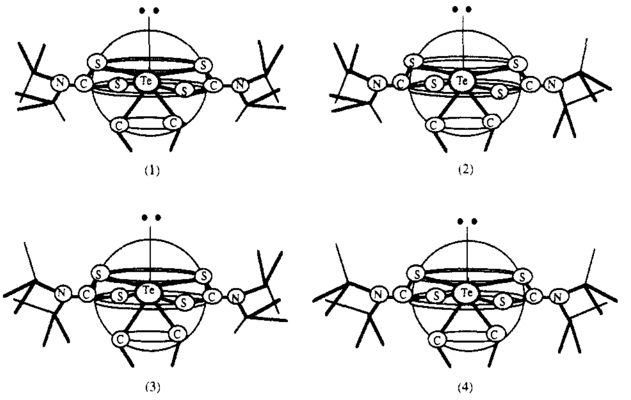

Figure 6. The four possible configurational isomers for $C_8H_8Te(^iPrdtc)_2$.

Therefore the spectral changes observed for $C_8H_8Te(^iPrdtc)_2$ can be explained by a stepwise "freezing" on the NMR time scale of various intramolecular exchange processes. Thus the ^{13}C spectrum of $C_8H_8Te(^iPrdtc)_2$ at room temperature which shows two broad signals for the methine carbon of the isopropyl group probably reflects the slowing of monodentate–bidentate exchange of the dithiocarbamate ligands. At −90 °C all carbon resonances are sharp, implying that the isopropyl group rotation is slow on the NMR time scale due to steric gearing of the geminal isopropyl groups. The latter process may be assisted by the possibility of a methine hydrogen–sulfur interaction which would contribute to the rotational barrier.[43,44] Observation of three ^{125}Te resonances at −90 °C implies that there are three conformers in solution with the most likely geometry based on the 1:2:2:2 structure containing a stereochemically active lone electron pair. The solution geometry is thus probably very similar to the solid-state structure observed for **1**. Restricted rotation of isopropyl groups gives rise to the four possible conformational isomers illustrated in Figure 6. Conformers 1 and 4 are superimposable by a rotation and therefore identical. Conformers 2 and 3 are related by a center of symmetry making them enantiomers, but since their mirror images cannot be superimposed they are in fact diastereomers which could, in principle, give rise to different chemical shifts. If each conformer is of equal probability, three ^{125}Te resonances, of intensity ratio 1:2:1, should be observed. the fact that the observed intensity ratio is 1:2.8:1.6 implies that each conformer is not equally probable. This may occur because of the existence of a methine hydrogen–sulfur interaction (mentioned above) which renders the conformers energetically nonequivalent.

NMR Studies of Mixed-Dithiolate Complexes. The ^{125}Te spectrum at room temperature of a dichloromethane solution containing an equimolar mixture of **1** and **3** shows three resonances [$\delta(^{125}Te)$ −1066, −1098, −1121 ppm]. The two outer resonances are identified as due to the starting components, whilst the central resonance is assigned to the mixed-ligand species C_8H_8Te(Etdtc)(Etxan). Similarly when **3** and **2** are mixed, three ^{125}Te resonances of relative intensity 1:2:1 are observed with the central resonance assigned to the compound C_8H_8Te(Etxan)(Etdtp) (Table X). However, the ^{125}Te spectrum of an equimolar solution of **1** and **2** shows only a single resonance [$\delta(^{125}Te)$ −1060 ppm] which is assigned to the mixed-ligand species C_8H_8Te(Etdtc)(Etdtp). The compound C_8H_8Te(Etdc)(Etdtp) was subsequently isolated as yellow needles: mp 109–110 °C. As the temperature is lowered to −60 °C this resonance becomes a doublet due to coupling to phosphorus ($^2J_{Te-P}$ = 29 Hz). The ^{31}P spectrum at −60 °C

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Table XI. Selected Carbon-13 Data for Various Tellurium(IV) Dithiolate Complexes δ (^{13}C)

species	carbon number[d]							
	1	2	3	4	5	6		7
$C_8H_8Te(^iPrdtc)_2$								
(in chl at 30 °C)	44.1	140.7	127.2	130.4	200.4	52.3		20.3
						55.5		
(in chl at −40 °C)						50.8		19.6
						57.3		20.2
(in dcm at −90 °C)					194.5	48.3	54.7	17 br d
					196.1	49.3	56.0	
$C_8H_8Te(Etdtc)(Etdtp)$								
(in dcm at −80 °C)						48.7		11.0
						49.2		12.0
$C_8H_8Te(Etdtc)(^iPrdtp)$								
(in chl at 0 °C)	45.5	139.9	127.6	130.3	196.1	49.0		12.3
						72.3[a]		23.9
$C_8H_8Te(^iPrdtc)(Etdtp)$								
(in chl at 30 °C)	45.3	140.0	127.6	130.2	195.0	54.7		20.0
						63.1[a]		16.2[b]
$C_8H_8Te(^iPrdtc)(Etdtp)$								
(in chl at −60 °C)	43.9	139.1	127.4	130.1	191.0	50.6	51.9	18.1, 19.1
	44.8				193.3	58.2	59.1	20.4
						62.6		15.9
$C_8H_8Te(^iPrdtc)(^iPrdtp)$								
(in chl at 30 °C)	45.1	139.9	127.5	130.5	194.9	54.6 br d		20.1
						72.0[b]		23.9[c]
(in chl at −60 °C)	44.1				191.8	50.7	57.3	18.2
	44.9				144.1	51.8	58.3	19.3 br d
								20.5

[a] $^2J_{c-p} = 6$ Hz. [b] $^3J_{c-p} = 8$ Hz. [c] $^3J_{c-p} = 4$ Hz. [d] Carbon atom assignment given in Chart I.

contains a single resonance at $\delta(^{31}P)$ 99.3 ppm, with ^{125}Te satellites giving the same coupling constant as was observed in the ^{125}Te spectrum. Apparently tellurium–phosphorus coupling is not observed above −60 °C due to rapid intramolecular monodentate–bidentate exchange of the dithiophosphate ligand. It is interesting to note that the ^{125}Te spectrum of each of the complexes $C_8H_8Te(Etdtp)_2$ and $C_8H_8Te(^iPrdtp)_2$ in dichloromethane solution shows no sign of tellurium–phosphorus coupling at temperatures down to −110 °C, which indicates that monodentate–bidentate exchange of the dithiophosphate ligands in these two complexes is rapid at all accessible temperatures. At −80 °C the ^{13}C spectrum of $C_8H_8Te(Etdtc)(Etdtp)$ shows that each of the methyl [$\delta(^{13}C)$ 11.0, 12.0 ppm] and methylene [$\delta(^{13}C)$ 48.7, 49.2 ppm] carbon atoms of the dithiocarbamate group are nonequivalent.

Similar spectral changes are observed for the compound $C_8H_8Te(Etdtc)(^iPrdtp)$, prepared in situ from an equimolar ratio of $C_8H_8Te(Etdtc)_2$ and $C_8H_8Te(^iPrdtp)_2$ in chloroform solution. At room temperature a single ^{125}Te resonance is observed (Table X) which becomes a doublet at −60 °C due to coupling to phosphorus ($^2J_{Te-P} = 27$ Hz). The ^{13}C spectrum at 0 °C shows only one type of ethyl group for the dithiocarbamate ligand [$\delta(^{13}C)$ 12.3, 49.0 ppm] and only one type of isopropyl group for the dithiophosphate ligand [$\delta(^{13}C)$ 23.9, 72.3 ppm]. The benzylic methylene carbon atoms adjacent to the tellurium atom give a single sharp resonance. Three aromatic ^{13}C resonances are observed (Table XI) which suggests that the C_8H_8 group is bisected by an axis of symmetry. At −60 °C each of the methyl and methylene groups of the dithiocarbamate ligand become nonequivalent [$\delta(^{13}C)$ 11.5, 12.4 ppm and 48.7, 49.2 ppm, respectively]. No changes occur for the isopropyl ^{13}C resonances of the dithiophosphate ligand nor for the aromatic and benzylic resonances.

When equimolar quantities of $C_8H_8Te(^iPrdtc)_2$ and $C_8H_8Te(Etdtp)_2$ are dissolved in chloroform solvent, the ^{125}Te spectrum indicates that $C_8H_8Te(^iPrdtc)(Etdtp)$ is the major species in solution [$\delta(^{125}Te)$ −1057 ppm] together with small amounts of the initial components. At 0 °C the ^{125}Te spectrum consists of a single broad resonance of $\delta(^{125}Te)$ −1059 ppm ($w_{1/2} = 130$ Hz). At −30 °C this resonance splits into two broad signals [$\delta(^{125}Te)$ −1050, 1069 ppm], and at −60 °C the ^{125}Te spectrum consists of two doublets ($J = 30$ Hz separated by 600 Hz) of equal intensity. The smaller splitting of 30 Hz is assigned to two bond coupling, $^2J_{Te-P}$. It is not immediately clear whether the two doublets are related. The ^{31}P resonance for $C_8H_8Te(^iPrdtc)(Etdtp)$ is broad at room temperature, probably as a consequence of the ligand exchange process occurring at a rate which approximates the NMR time scale. The ^{31}P spectra at −30 °C and −60 °C are identical and each consists of a single resonance at $\delta(^{31}P)$ 101.5 ppm due to $C_8H_8Te(^iPrdtc)(Etdtp)$. NMR spectra for the above mixture in dichloromethane (instead of chloroform) are more informative.

The ^{125}Te spectrum of $C_8H_8Te(^iPrdtc)(Etdtp)$ in dichloromethane solution at room temperature contains a single resonance [$\delta(^{125}Te)$ −1072 ppm; $w_{1/2} = 70$ Hz] which broadens considerably at −20 °C; at −40 °C it resolves into two broad but well separated signals of unequal intensities [$\delta(^{125}Te)$ −1069, −1090 ppm], and at −80 °C each of these splits into a doublet, $^2J_{Te-P} = 27$ Hz. It is the unequal intensity of the doublets which shows that the original two doublets, observed in chloroform, are not magnetically related but suggests that they are due to different conformers of the same molecule. The ^{31}P resonance of $C_8H_8Te(^iPrdtc)(Etdtp)$ is a singlet at temperatures above −80 °C but at −80 °C splits into two well-resolved resonances [$\delta(^{31}P)$ 100.1, 100.3 ppm] with an intensity ratio equal to that observed for the two ^{125}Te resonances. It is interesting to note that changing solvents from chloroform to dichloromethane causes changes in the conformer proportion and the temperature at which these conformers are static on the NMR time scale.

The room temperature ^{13}C spectrum of $C_8H_8Te(^iPrdtc)(Etdtp)$ in chloroform is deceptively simple (Table XI) and implies that both the dithiocarbamate and dithiophosphate ligands are undergoing rapid intramolecular monodentate–bidentate exchange. However at −60 °C the diethyldithiophosphate ligand gives two ^{13}C resonances [$\delta(^{13}C)$ 15.9 ppm, $^3J_{C-P} = 10$ Hz; 62.6 ppm, $^2J_{C-P} = 6$ Hz]. The methyl carbon atoms of the diisopropyldithiocarbamate ligand give three resonances [$\delta(^{13}C)$ 18.1, 19.1, 20.4 ppm] due to the nonequivalent methyl carbons in each of the two conformers (Figure 7). The resonance at $\delta(^{13}C)$ 19.1 ppm is not symmetrical and appears to result from the superposition of two resonances. The methine carbon atoms display four well-resolved resonances [$\delta(^{13}C)$ 50.6, 51.9, 58.2, 59.1 ppm]. The dithio carbon atom (i.e., S_2C-) shows two resonances [$\delta(^{13}C)$ 191.0, 193.3 ppm] of equal intensity, corresponding to the two possible conformations of the diisopropyldithiocarbamate ligand in $C_8H_8Te(^iPrdtc)(Etdtp)$. The benzylic carbons adjacent to tellurium also give two resonances [$\delta(^{13}C)$ 43.9, 44.8 ppm] once again, due to the two possible conformers (Figure 7). The aromatic carbon atoms give

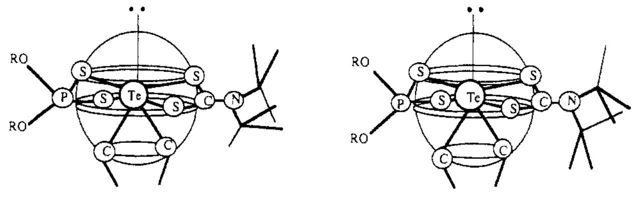

Figure 7. Two possible conformers for each of the compounds C$_8$H$_8$Te(^{i}Prdtc)(^{i}Prdtp) and C$_8$H$_8$Te(^{i}Prdtc)(Etdtp).

apparently only three resonances (Table XI).

Similar spectral changes are observed for C$_8$H$_8$Te(^{i}Prdtc)(^{i}Prdtp) formed in an equimolar mixture of C$_8$H$_8$Te(^{i}Prdtc)$_2$ and C$_8$H$_8$Te(^{i}Prdtp)$_2$ in chloroform. At room temperature a single ^{125}Te resonance is observed [$\delta(^{125}$Te) −1062 ppm]. The ^{125}Te spectrum of C$_8$H$_8$Te(^{i}Prdtc)(^{i}Prdtp) consists of two broad resonances [$\delta(^{125}$Te) −1074, −1055 ppm] at −30 °C which sharpen at −60 °C, each becoming a doublet [$\delta(^{125}$Te) −1054 ppm, $^2J_{\mathrm{Te-P}}$ = 29 Hz; −1073 ppm, $^2J_{\mathrm{Te-P}}$ = 29 Hz]. At −80 °C these two doublet resonances broaden and are of unequal intensity. The ^{13}C spectrum at room temperature shows one benzylic and three aromatic ^{13}C resonances (Table XI). The diisopropyldithiophosphate ligand gives doublet ^{13}C resonances for the methine and methyl carbon atoms due to phosphorus-31 coupling. The diisopropyldithiocarbamate ligand shows one dithio (i.e., S$_2$*C*-) ^{13}C resonance. The resonance due to the methyl groups of the dithiocarbamate ligand is a singlet [$\delta(^{13}$C) 20.1 ppm], but the methine carbons give two very broad resonances centered at $\delta(^{13}$C) 54.6 ppm, indicating that the diisopropyldithiocarbamate ligand is static (i.e., bidentate) on the NMR time scale.

At −60 °C the aromatic and the diisopropyldithiophosphate signals are unchanged from those at room temperature. However the ^{13}C resonance due to the benzylic carbon atoms adjacent to the tellurium atom is split into two signals as is the dithio (i.e., S$_2$*C*-) carbon resonance of the diisopropyldithiocarbamate ligand (Table XI). Apparently the methyl groups as well as being anisochronous due to restricted N–C bond rotation are in different environments in each of the conformers. The four methyl resonances are too close to be well resolved; the outer signals are observed [$\delta(^{13}$C) 18.2, 20.5 ppm], but the inner two are almost superimposed [$\delta(^{13}$C) 19.3 ppm] giving rise to a distorted triplet. The methylene carbon resonances are well resolved, and all four are observed [$\delta(^{13}$C) 50.7, 51.8, 57.3, 58.8 ppm]. Surprisingly, the ^{31}P spectrum is a singlet at −60 °C [$\delta(^{31}$P) 97.9 ppm] instead of the expected two resonances due to the presence of two conformers indicated by the ^{125}Te spectrum. Since only one ^{31}P resonance is observed at −60 °C, the variable-temperature NMR experiment was repeated in dichloromethane solvent to extend the accessible lower temperature range. The ^{31}P spectrum now contains two resonances [$\delta(^{31}$P) 97.5, 97.3 ppm] of intensity ratio equal to that observed for the ^{125}Te resonances.

The similarity of the NMR spectral changes observed for C$_8$H$_8$Te(^{i}Prdtc)(^{i}Prdtp) and C$_8$H$_8$Te(^{i}Prdtc)(Etdtp) can be explained in terms of the spatial arrangement of the diisopropyldithiocarbamate ligand, with use of similar arguments as were presented for the case of C$_8$H$_8$Te(^{i}Prdtc)$_2$. Two nonsuperimposable conformers (i.e., diastereoisomers) appear to be present in solution (Figure 7) which give rise to different ^{125}Te resonances.

Conclusions

The solid-state geometries of **1**, **2** and **3** are in each case determined by the presence of lone electron pairs at the tellurium(IV) centers. The secondary bonding apparent in **2** and **3** results from the fact that the tellurium(IV) center in these two complexes is coordinately unsaturated. The degree of secondary bonding implies that the dithiolate ligand donor strength is in the order dtc > dtp > xan. It has been shown for the first time that at low temperatures it is possible to slow, on the NMR time scale, intramolecular monodentate–bidentate exchange, of the dithiocarbamate ligands in solutions of the complexes C$_8$H$_8$Te(Rdtc)$_2$ (R = Et, ^{i}Pr). In the case of R = ^{i}Pr, slow intramolecular monodentate–bidentate exchange and slow bond rotation of isopropyl groups (i.e., static gearing) results in the observation of multiple ^{125}Te resonances due to different conformers, illustrating the utility of ^{125}Te NMR for the determination of solution structures. The NMR experimental data are supportive of isobidentically chelated dialkyldithiocarbamate and dialkyldithiophosphate ligands in the mixed dithiolate complexes, C$_8$H$_8$Te(Rdtc)(Rdtp) (R = Et, ^{i}Pr), which result in seven-coordinate geometries at low temperatures. Furthermore, the structures inferred in solution appear to be similar to those determined directly in the solid state, and all appear to contain a stereochemically active lone electron pair. It is interesting to note that the compound C$_8$H$_8$Te(^{i}Prdtc)$_2$ and the mixed-dithiolate complexes show statistical distribution of conformer populations in chloroform but not in dichloromethane solution.

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Registry No. **1**, 116052-72-3; **2**, 116052-73-4; **3**, 116052-74-5; C$_8$H$_8$Te(^{i}Prdtc)$_2$, 116052-75-6; C$_8$H$_8$Te(^{i}Prdtp)$_2$, 116052-76-7; C$_8$H$_8$Te(^{i}Prxan)$_2$, 116052-77-8; C$_8$H$_8$Te(Etdtc)(Etxan), 116052-78-9; C$_8$H$_8$Te(Etdtp)(Etxan), 116052-79-0; C$_8$H$_8$Te(Etdtc)(Etdtp), 116052-80-3; C$_8$H$_8$Te(Etdtc)(^{i}Prdtp), 116052-81-4; C$_8$H$_8$Te(^{i}Prdtc)(Etdtp), 116052-82-5; C$_8$H$_8$Te(^{i}Prdtc)(^{i}Prdtp), 116052-83-6; C$_8$H$_8$Te(Etdtc)(^{i}Prdtc), 116052-84-7; C$_8$H$_8$Te(Etdtp)(^{i}Prdtp), 116052-85-8; C$_8$H$_8$Te(Etxan)(^{i}Prxan), 116052-86-9; C$_8$H$_8$TeI$_2$, 66149-48-2; NaEtdtc, 148-18-5; KEtdtp, 3454-66-8; KEtxan, 140-89-6; Na^{i}Prdtc, 4092-82-4; K^{i}Prdtp, 3419-34-9; K^{i}Prxan, 140-92-1.

Supplementary Material Available: Unit cell packing diagrams, Tables S-1–S-XV listing anisotropic temperature factors, hydrogen atom coordinates and their isotropic temperature factors, hydrogen atom bond lengths and angles, phenylic bond lengths and angles, and mean planes and nonbonding separations (23 pages); tables of observed and calculated structure factors for compounds **1**, **2**, and **3** (48 pages). Ordering information is given on any current masthead page.