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$\Delta^{4,4'}$-4-CHALCOGENAPYRANYL-4*H*-CHALCOGENAPYRANS

SYNTHESIS, ELECTROCHEMICAL OXIDATION, AND ESR INVESTIGATIONS OF RADICAL-CATION STATES

MICHAEL R. DETTY,* JAMES W. HASSETT,
BRUCE J. MURRAY and GEORGE A. REYNOLDS
Research Laboratories, Eastman Kodak Company, Rochester, NY 14650, U.S.A.

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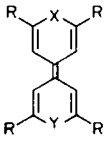
Abstract—The O-, S-, Se- and Te-containing $\Delta^{4,4'}$-2,2',6,6'-tetramethyl-, -tetra-*t*-butyl- and -tetraphenyl-4-(chalcogenapyranyl)-4*H*-chalcogenapyrans were prepared from the corresponding chalcogenapyran-4-ones. The thia-, selena- and tellurapyran-4-ones were prepared by sodium borohydride reduction of the appropriate chalcogen and addition of the disodium chalcogenide to a 1,4-diyn-3-one. The comparative electrochemistry of all three series was examined by cyclic voltammetry. Within each series the first oxidation (E_1) became more difficult with increasing chalcogen size. The radical-cation states of the tetra-*t*-butyl analogues were examined by ESR. The O and S analogues gave well-defined five-line spectra, but the Se and Te analogues gave broad single lines. The *g* value increased with increasing size of the heteroatom. A linear correlation exists between *g* value and spin–orbit coupling constants λ for the chalcogens, suggesting that the electron densities on the heteroatoms are similar in each heteroatom analogue.

In donor molecules in which a group 6a atom (O, S, Se, or Te) is in conjugation with a carbon π system, the oxidation potential of the donor system should be influenced by two different trends. As the group 6a atom becomes more electropositive, loss of an electron from the heteroatom should become more facile and the oxidation potential more cathodic. However, as the size of the heteroatom increases, overlap of the orbitals of the group 6a atom with those of the carbon π framework would become less efficient and π ionization will become more difficult, making the oxidation potential more anodic and the unpaired spin more localized on the heteroatom.

The $\Delta^{4,4'}$-4-chalcogenapyranyl-4*H*-chalcogenapyrans (**1–4**) (R = Ph, *t*-Bu, and Me) are characterized electrochemically by two reversible one-electron oxidations to give the radical-cations and dication states.[1–4] Complexes of the neutral donors, the radical-cations and the dications are semiconducting.[4] The stability of the radical-cations and dications is believed to be due to formation of aromatic sextets upon oxidation.[5] This implies that π-delocalized radical-cation systems are formed.



1, X=Y=O
2, X=Y=S
3, X=Y=Se
4, X=Y=Te

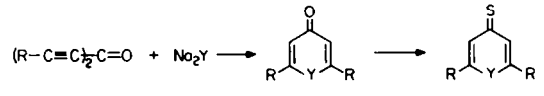
The radical-cation states of the chalcogenapyranylchalcogenapyrans have not been systematically investigated spectroscopically for subtle changes in electron densities that might be expected to occur with heteroatoms of markedly different sizes and electronegativities. The conductivities of chalcogenapyranylchalcogenapyran complexes have been systematically examined,[4–6] although single-crystal conductivities have been measured for only the oxygen- and sulphur-containing systems.

We report here our syntheses of chalcogenapyranylchalcogenapyrans (**2–4**), the electrochemical oxidations of **1–4** (R = Ph, *t*-Bu and Me) by cyclic voltammetry and thin-layer coulometry, and the ESR spectra of several radical-cations in this series. The trends observed show that oxidation potential is a function of the heteroatom in the ring system, although electron delocalization in the radical-cations of **1–4** appears to be quite similar.

RESULTS AND DISCUSSION

Preparation of chalcogenapyranylchalcogenapyrans

The chalcogenapyranylchalcogenapyrans were prepared as indicated in Scheme 1. The elemental chalcogens were reduced with sodium borohydride in 0.5 M sodium ethoxide in ethanol to the corresponding disodium chalcogenide. The addition of the appropriate diynone gave the chalcogenapyranones **5–7**. The chalcogenapyranones were converted to the corresponding thiones,[7] **8–10**, with the Lawesson reagent[8] in hot toluene. Copper-assisted dimerization of the thiones in refluxing toluene gave the chalcogenapyranylchalcogenapyrans (**2–4**) listed in Table 1. The sodium borohydride reductions of sulphur, selenium and tellurium and subsequent addition to 1,4-diyn-3-ones represent significant improvements in yields over the literature methods.[2,7]



5, Y=S
6, Y=Se
7, Y=Te

8, Y=S
9, Y=Se
10, Y=Te

Scheme 1.

Table 1. Preparation of $\Delta^{4,4'}$-chalcogenapyranyl-4*H*-chalcogenapyrans

Compound	R	Yield (%)*	M.p. (°)	FDMS [*m/z* (empirical formula)]
2b	*t*-Bu	71	257–258	416 ($C_{26}H_{40}S_2$)
3a	Ph	65	297–299†	592 ($C_{34}H_{24}{}^{80}Se_2$)
3b	*t*-Bu	39	260–263	512 ($C_{26}H_{40}{}^{80}Se_2$)
3c	Me	45	210–212‡	344 ($C_{14}H_{16}{}^{80}Se_2$)
4a	Ph	66	273–274	692 ($C_{34}H_{24}{}^{130}Te_2$)
4b	*t*-Bu	80	273–275	612 ($C_{26}H_{40}{}^{130}Te_2$)
4c	Me	32	212–217 (dec.)	444 ($C_{14}H_{16}{}^{130}Te_2$)

* Isolated yield.
† Lit.[2] m.p. 299–302°.
‡ Lit.[2] m.p. 180°.

Table 2. Oxidation potentials of $\Delta^{4,4'}$-chalcogenapyranyl-4*H*-chalcogenapyrans*

Compound	X	R	E_1 (V)		E_2 (V)		ΔE (V)
			E_{p_a}	E_{p_c}	E_{p_a}	E_{p_c}	
1a	O	Ph	0.20	0.10	0.52	0.42	0.32
2a	S	Ph	0.27	0.17	0.46	0.36	0.19
3a	Se	Ph	0.38	0.28	0.54	0.43	0.15
4a	Te	Ph	0.39	0.28	0.54	0.43	0.15
1b	O	*t*-Bu	0.16	0.050	0.595	0.47	0.43
2b	S	*t*-Bu	0.14	0.08	0.41	0.335	0.26
3b	Se	*t*-Bu	0.235	0.165	0.48	0.40	0.24
4b	Te	*t*-Bu	0.285	0.195	0.425	0.345	0.15
1c	O	Me	0.08	0.00	0.46	0.38	0.38
2c	S	Me	0.13	0.04	0.38	0.30	0.25
3c	Se	Me	0.15	0.09	0.32	0.26	0.17
4c	Te	Me	0.27	0.17	0.40	0.32	0.14

* Potentials are vs a saturated calomel reference electrode (saturated aqueous NaCl) at glassy carbon with a scan rate of 100 mV/sec. Sample concentration was $\sim 5 \times 10^{-4}$ M with 0.2 M tetrabutylammonium fluoroborate as supporting electrolyte in dichloromethane.

Electrochemical oxidation of bipyranylidenes (**1–4**)

The first (E_1) and second (E_2) oxidation potentials (vs saturated calomel electrode, SCE) as determined by cyclic voltammetry for chalcogenapyranylchalcogenapyrans **1–4** (R = Ph, *t*-Bu and Me) are compiled in Table 2. A plot of oxidation potential as a function of ionization potential[9] (I_p) of the group 6a atom as shown in Fig. 1 for E_1 reveals that E_1 becomes increasingly less anodic as I_p for the group 6a atom increases. The variation in E_1 can be rationalized in terms of the overlap of the heteroatom orbitals with the carbon π framework. Although increasing electropositive character (smaller I_p) should facilitate oxidation, the poorer heteroatom overlap with the carbon π framework as the heteroatom becomes larger makes π ionization increasingly difficult and this factor appears to dominate. Both the electronegativity and size differences among the group 6a atoms appear to influence the oxidation of the radical-cation to the dication. The former facilitates oxidation by helping to overcome the coulombic attraction for the second electron and the latter contributes a more anodic oxidation through poorer overlap with the carbon π framework. The net effect of these trends is to narrow the gap between E_1 and E_2 (ΔE) as the group 6a atom becomes larger. The 0.15 V separation between E_1 and E_2 for tellurapyranyltellurapyrans (**4**) is achieved for pyranylpyrans (**11**) and thiapyranylthiapyrans (**12**) only when $n \geqslant 3$.[10] Tellurapyranyltellurapyrans

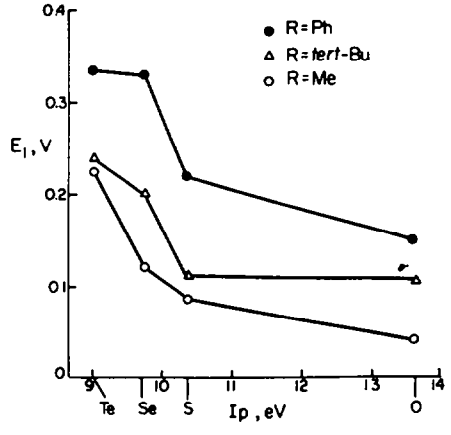
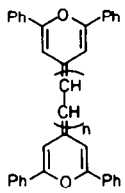


Fig. 1. Plot of first oxidation potential (E_1) vs heteroatom ionization potential (I_p) for chalcogenapyranylchalcogenapyrans (**1–4**). The connecting lines show related points and have no other significance.

should allow more ready access to two-electron donors.[11]



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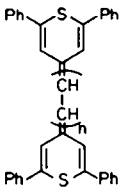
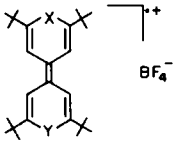


12

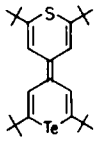
ESR studies of radical-cations

Experimentally, the degree of localization or delocalization of the unpaired electron in the radical-cations of **1**–**4** should be reflected in the ESR spectra of these species. Changes in spin density within the carbon framework should be indicated by changes in the magnitude of the coupling constants of the unpaired spin with the ring protons (a_H).[12] The ESR spectra of different polyiodide complexes of thiapyranyl-thiapyran (**2a**) in the solid state have been reported as broad single lines.[13] We were interested in ESR studies of complexes of chalcogenapyranylchalcogenapyrans that would allow study of intramolecular as opposed to intermolecular interactions. Thus, solution ESR spectra were determined for these systems.

The radical-cations of the *t*-butyl derivatives of the chalcogenapyranylchalcogenapyrans (**1b**, **2b**, **3b**, **4b**) were generated in a coulometric flow reactor that was a modification of a design by Miner and Kissinger.[14] The working electrode was reticulated vitreous carbon and the radical-cations were generated in dichloromethane with 0.2 M tetrabutylammonium fluoroborate as supporting electrolyte. The ESR spectra were recorded as the oxidized sample flowed through a flat (0.5 mm) quartz ESR cell.



13, X = Y = O
14, X = Y = S
15, X = Y = Se
16, X = Y = Te
17, X = S, Y = Te



18

The first-derivative ESR spectra for radical-cations **13**–**16** are shown in Figs 2 and 3; values of g and a_H are recorded in Table 3. Line widths and g values increase in the sequence O < S < Se < Te. Interestingly, a_H is larger in **14** than in **13**. The ESR spectra of **15** and **16** are featureless single lines with line widths of 1.26 and 4.06 G, respectively. The ESR spectrum of **13** is a well-defined five-line spectrum. The ESR spectrum of **14** also has five lines with several of lesser intensities also discernible. We have assumed that these other lines are due to an impurity and are not from **14**.

The ESR spectrum of **15** has two less intense lines of 1.28 G line width and a separation of 10.99 G. These signals are consistent in intensity with the expected signals of the ~7% abundance of ^{77}Se, magnetically active with spin 1/2.

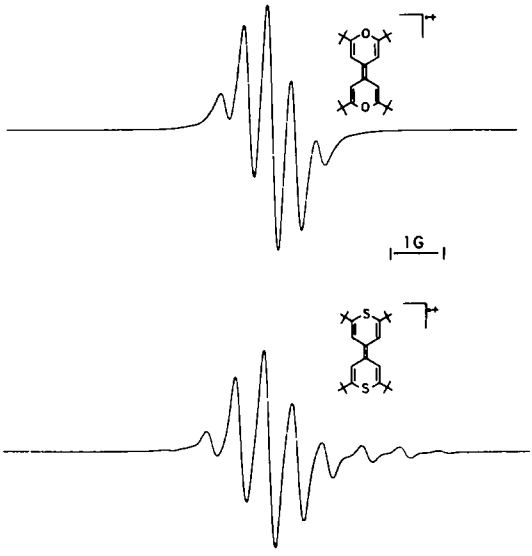


Fig. 2. First-derivative ESR spectra for radical-cations **13** and **14**.

The ESR spectrum of **16** has, in addition to the single broad signal for **16**, a weaker signal at $g = 2.027$ with line width of 2.02 G and a still weaker signal at $g = 2.009$. These signals can be tentatively assigned to radical-cations **17** and **14**, respectively. These products arise from the corresponding chalcogenapyranyl-chalcogenapyrans **18** and **2b**, which are produced in small quantities by tellurium–sulphur exchange during the synthesis of **4b**.[3] Both the g value and the line width of **17** would be expected to be intermediate between those of **14** and **16**.

The increasing line widths and increasing g values are related to the spin–orbit coupling, which increases with increasing atomic number within the periodic table.[12]

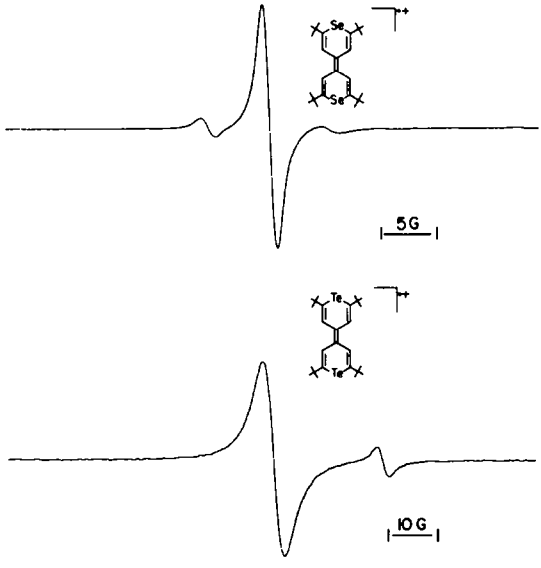


Fig. 3. First-derivative ESR spectra for radical-cations **15** and **16**.

Table 3. ESR data for $\Delta^{4,4'}$-2,2',6,6'-tetra-*t*-butylchalcogenapyranyl-4*H*-chalcogenapyran radical-cations

Radical-cation	Chalcogen	g	$a_{H'}$ (G)	λ (eV)*
13	O	2.008	0.438	0.004
14	S	2.009	0.532	0.05
15	Se	2.024	†	0.29
16	Te	2.041	‡	0.60
17	S, Te	2.027	§	0.325‖

* See lit.[12,14]
† Single broad line with line width of 1.25 G.
‡ Single broad line with line width of 4.06 G.
§ Single broad line with line width of 2.02 G.
‖ $\bar{\lambda}$ of λ_S and λ_{Te}.

The spin–orbit coupling constants (λ) for positively charged Se and Te are available[15] and for S and O they are assumed to be close to their neutral-atom values.[12,15]

Although the g values for **13–17** are quite different from one another as well as from that of the free electron ($g = 2.0023$),[16] a plot of g value vs the spin–orbit coupling constant should give a linear regression if the spin populations on the heteroatoms in **13–17** are approximately constant.[12] A least-squares plot of the data gives $g = 2.0073 + 0.0571\ \lambda$ (λ is in eV) for **13–17**. The correlation coefficient is 0.999 (Fig. 4).

The radical-cation of **4a** was also prepared. We had hoped that increased delocalization into the phenyl rings would allow resolution of fine structure. However, the ESR spectrum of this cation was a single broad line with $g = 2.029$.

In an attempt to evaluate the degree of delocalization of the unpaired spin into one or both rings, a doubly ^{125}Te-labelled sample of **16** was prepared as shown in Scheme 2. The ESR signal of the labelled material should be split into a two- or three-line spectrum by coupling of the free spin to one or both spin-1/2 ^{125}Te nuclei. Unfortunately, the observed ESR signal was a single broad line with $g = 2.04$. Either the triplet splitting is large and the smaller lines too weak to detect or the ^{125}Te coupling is smaller than the ^{77}Se coupling and is buried in the single line.

The ESR data for the different radical-cations do not allow a detailed analysis of the spin densities at each atom in the ring system. The effects of spin–orbit coupling are observed in the increasing g values and line widths with increasing atomic number of the heteroatoms. The linearity of the plot of g value vs the spin–orbit coupling constant suggests that the four different radical-cations have similar spin-density distributions between the carbon π framework and the two heteroatoms. Thus, the substitution of heteroatoms in the chalcogenapyranylchalcogenapyrans does not lead to greatly different radical-cation structures.

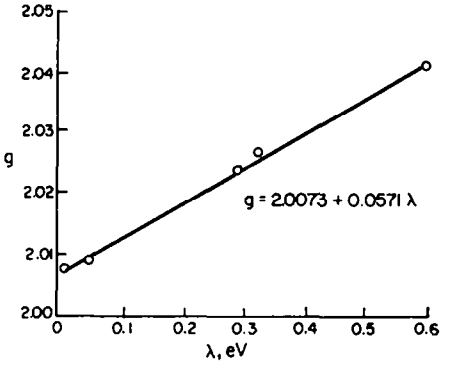
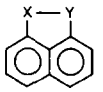


Fig. 4. Plot of g value vs heteroatom spin–orbit coupling constant (λ) for radical-cations **13–17**.

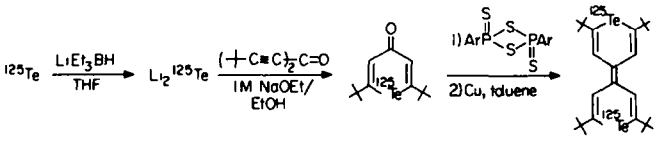
The radical-cations of 1,8-chalcogen-bridged naphthalenes (**19**) have been examined by UV-photoelectron spectroscopy and by ESR spectroscopy.[12] The unpaired spin in these systems appears to be localized in the naphthalene π system on the basis of spin populations and the molecular orbital picture developed to explain the photoelectron spectra. A plot of g value vs spin–orbit coupling (λ) of the heteroatoms gave the dependence $g = 2.00126 + 0.16421\ \lambda$. The radical-cations **13–16** show a much smaller dependence of g value on λ ($g = 2.0073 + 0.0571\ \lambda$), suggesting that the unpaired spin in these systems is even more delocalized than in the radical-cations of **19**.



19

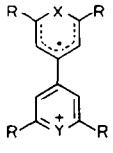
XY = SS, SSe, STe, SeSe, SeTe

In summary, all of the radical-cations of chalcogenapyranylchalcogenapyrans studied have similar elec-



Scheme 2.

tronic structures in spite of the fact that the heteroatoms involved have quite different sizes and electronegativities. The unpaired spin appears to be localized in the carbon π system. The positive charge is stabilized by the formation of an aromatic sextet as in **20**, implying that overlap of the heteroatoms with the carbon π system is important even with Se and Te. The electrochemical oxidation of the chalcogenapyranyl-chalcogenapyrans demonstrates that such overlap is important in that oxidation becomes more difficult as the heteroatom becomes larger. This is contrary to what one would expect on the basis of I_p for the heteroatoms. However, once ionized, the resulting radical-cations are quite delocalized.



20

EXPERIMENTAL

M.ps were determined on a Thomas–Hoover m.p. apparatus and are corrected. ^{1}H-NMR spectra were recorded on a Beckman IR 4250 instrument. UV–visible spectra were recorded on a Cary 17 spectrophotometer. Tellurium powder, Te shot and Se shot were purchased from Ventron. Solvents were obtained from Kodak Laboratory Chemicals and were dried over 3 Å molecular sieves before use or were used as received. Microanalyses were performed at Kodak on a Perkin–Elmer C, H, and N analyser. Tellurium and Se analyses were performed by atomic absorption spectroscopy with ±1% accuracy. Pyranylpyran (**1**) and thiapyranyl-thiapyrans (**2a** and **2c**) were prepared by lit.[1] procedures.

Electrochemical procedures. A Princeton Applied Research model 173 potentiostat/galvanostat and a model 175 universal programmer were used for the electrochemical measurements. The working electrode for cyclic voltammetry was glassy carbon, obtained from Princeton Applied Research, model 90021. The coulometric flow reactor, used for generation of electrolysis products, was a modification of a design by Miner and Kissinger.[14] The working electrode was reticulated vitreous carbon (RVC) porosity 100, grade 4, obtained from Normar Industries. A Ag-AgO quasi-reference electrode was used in the flow cell.

All samples were run in J. T. Baker HPLC-grade CH_2Cl_2 that had been stored over Kodak type 3 Å molecular sieves. Electrometric-grade tetrabutylammonium fluoroborate ($TBABF_4$), obtained from Southwestern Analytical Chemicals and dried at 80° overnight, was used as supporting electrolyte at 0.2 M concentration. Argon was used for sample deaeration.

The exit of the electrochemical flow cell was connected to a flat (0.5 mm) ESR cell (Wilmad Glass Co.) with Omnifit 1/16 in Teflon tubing and Tefzel connectors. The ESR spectra of the oxidation products were obtained on a Bruker ER 200D-SRC 100 kHz spectrometer at room temp (~25°).

The oxidation products were generated by holding the RVC working electrode at a potential beyond the first oxidation wave of the samples but before the onset of the second wave, while the deaerated sample solns flowed through the cell. With gravity flow, the flow rate through the ESR cell was 2–3 ml/min.

General procedure for the preparation of chalcogenapyran-4-ones. Preparation of 2,6-*diphenyltellurapyran-4-one* (**7a**). A 1 l. flask equipped with a water-cooled reflux condenser, a magnetic stirring bar and a dry-N_2 inlet was charged with 12.76 g (0.100 mol) of Te shot and 300 ml of 0.5 M NaOEt in EtOH. $NaBH_4$ (3.80 g, 0.100 mol) was added in three portions at 15 min intervals (mildly exothermic) to a gently refluxing mixture. After the final addition, the mixture was stirred at ambient temp for 2.0 hr until a clear colourless soln was obtained. 1,5-Diphenyl-1,4-pentadiyn-3-one (23.0 g, 0.100 mol) was dissolved in 200 ml of 0.05 M NaOEt in EtOH and was immediately added in one portion to the colourless soln of disodium telluride. The soln was stirred for 1 hr at ambient temp. The mixture was poured into 1 l of H_2O. The product was extracted with CH_2Cl_2 (3 × 250 ml). The combined organic extracts were washed with H_2O (250 ml), 10% NH_4Cl aq (250 ml) and brine (250 ml), dried over Na_2SO_4, and concentrated. The residue was purified by chromatography on silica gel, eluted with 10% EtOAc in CH_2Cl_2, to give, after recrystallization from MeCN, 24.1 g (67%) of **7a** as a yellow crystalline solid: m.p. 127–129° (lit.[3] m.p. 127.5–129°); ^{1}H-NMR ($CDCl_3$): δ 7.47 (m, 10H), 7.31 (s, 2H); IR ν_{max}^{KBr} cm^{-1}: 1570, 1550, 1430, 1310, 902, 870, 768, 755, 698; field-desorption mass spectrum (FDMS): *m/z* 362 ($C_{17}H_{12}O^{130}Te$). *For compound* **7b**. Yield 66%; m.p. 83.5–84°; ^{1}H-NMR ($CDCl_3$): δ 6.90 (s, 2H), 1.33 (s, 18H); IR ν_{max}^{KBr} cm^{-1}: 2985, 1600, 1575, 1330, 1275, 895; FDMS: *m/z* 322 ($C_{13}H_{20}O^{130}Te$). Anal.: calc. for $C_{13}H_{20}OTe$: C, 48.8; H, 6.3; Te, 39.9%; found: C, 48.9; H, 6.4; Te, 38.5%. *For compound* **7c**. Yield 37%; m.p. 95–97°; ^{1}H-NMR ($CDCl_3$): δ 6.74 (q, 2H, J < 1 Hz), 2.44 (d, 6H, J < 1 Hz); IR ν_{max}^{KBr} cm^{-1}: 2985, 1600, 1563, 1290, 905, 881, 855; FDMS: *m/z* 238 ($C_7H_8O^{130}Te$). Anal.: calc. for C_7H_8OTe: C, 35.7; H, 3.3; Te, 53.3%; found: C, 35.7; H, 3.4; Te, 54.1%. *For compound* **6a**. Yield 70%; m.p. 147–148° (lit.[3] m.p. 147–148°); ^{1}H-NMR ($CDCl_3$): δ 7.50 (m, 10H), 7.27 (s, 2H); IR ν_{max}^{KBr} cm^{-1}: 3050, 1580, 1560, 1360, 910, 875, 765, 755, 696. *For compound* **6b**. Yield 70%; m.p. 98–102°; ^{1}H-NMR ($CDCl_3$): δ 6.98 (s, 2H), 1.38 (s, 18H); IR ν_{max}^{KBr} cm^{-1}: 2970, 1615, 1340, 881; FDMS: *m/z* 272 ($C_{13}H_{20}O^{80}Se$). Anal.: calc. for $C_{13}H_{20}OSe$: C, 57.6; H, 7.4; Se, 29.1%; found: C, 57.6; H, 7.5; Se, 30.0%. *For compound* **6c**. Yield 56%; m.p. 83.5–86.5°; ^{1}H-NMR ($CDCl_3$): δ 6.83 (q, 2H, J < 1 Hz), 2.45 (d, 6H, J < 1 Hz); IR ν_{max}^{KBr} cm^{-1}: 1628, 1586, 1381, 886; FDMS: *m/z* 188 ($C_7H_8O^{80}Se$). Anal.: calc. for C_7H_8OSe: C, 44.9; H, 4.3; Se, 42.2%; found: C, 44.8; H, 4.3; Se, 42.0%. *For compound* **5b**. Yield 69%; m.p. 96–98°; ^{1}H-NMR ($CDCl_3$): δ 6.95 (s, 2H), 1.41 (s, 18H); IR ν_{max}^{KBr} cm^{-1}: 2975, 1620, 1350, 881, 731; FDMS: *m/z* 224 ($C_{13}H_{20}OS$). Anal.: calc. for $C_{13}H_{20}OS$: C, 69.6; H, 9.0; S, 14.3%; found: C, 69.9; H, 9.0; S, 14.1%.

General procedure for the preparation of chalcogenapyran-4-thiones. Preparation of 2,6-*diphenyltellurapyran-4-thione* (**10a**). A mixture of **7a** (3.60 g, 0.0100 mol) and the Lawesson reagent[8] (3.6 g) in 50 ml of toluene was heated at reflux under N_2 for 1 hr. The mixture was cooled to room temp and filtered through a pad of Celite. The Celite pad was washed with CH_2Cl_2 (2 × 50 ml), and the combined organics were concentrated. The residue was purified by chromatography on silica gel eluted with 10% EtOAc in CH_2Cl_2 to give 3.61 g (96%) of **10a**. M.p. 120–123° (lit.[3] m.p. 120–123°); ^{1}H-NMR ($CDCl_3$): δ 8.23 (s, 2H), 7.47 (m, 10H); IR ν_{max}^{KBr} cm^{-1}: 1545, 1480, 1068, 756, 690; FDMS: *m/z* 378 ($C_{17}H_{12}S^{130}Te$). *For compound* **10b**. Yield 96%; m.p. 129.5–131.5°; FDMS: *m/z* 338 ($C_{13}H_{20}OS^{130}Te$). Anal.: calc. for $C_{13}H_{20}OSTe$: C, 46.5; H, 6.0; S, 9.5; Te, 38.0%; found: C, 46.7; H, 6.1; S, 9.6; Te, 37.7%. *For compound* **10c**. Yield 63%; m.p. 107–110°. Anal.: calc. for C_7H_8STe: C, 33.4; H, 3.2; S, 12.7; Te, 50.7%; found: C, 33.2; H, 3.3; S, 12.4; Te, 49.8%. *For compound* **9a**. Yield 87%; m.p. 118–120° (lit.[2] m.p. 117°). *For compound* **9b**. Yield 79%; m.p. 161–162°; ^{1}H-NMR ($CDCl_3$): δ 7.98 (s, 2H), 1.52 (s, 18H). No parent ion was observed by FDMS. Several analyses were not within acceptable limits (high S, low C). The material was used as obtained. *For compound* **9c**. Yield 51%; m.p. 110–112° (lit.[2] m.p. 110°); FDMS: *m/z* 204 ($C_7H_8S^{80}Se$). Anal.: calc. for C_7H_8SSe: C, 41.7; H, 4.0; S, 15.8; Se, 38.9%; found: C, 41.2; H, 4.0; S, 15.3; Se, 39.5%. *For compound* **8b**. Yield 71%; m.p. 164–165°; FDMS: *m/z* 240 ($C_{13}H_{20}S_2$). Anal.: calc. for $C_{13}H_{20}S_2$: C, 64.9; H, 8.4%; found: C, 64.8; H, 8.3%.

Preparation of $\Delta^{4,4'}$*-2,2',6,6'-tetraphenyl-4-(tellurapyranyl)-4H-telluropyran* (**4a**). Thione (**10a**) (0.99 g, 2.6 mol) and copper powder (1.0 g) were slurried in 20 ml of toluene. The mixture was warmed for 4 hr under reflux and filtered through a 2.5 cm pad of Celite while hot. The Celite pad was washed with several portions of CH_2Cl_2, and the combined organic filtrates were concentrated. The residue was warmed in boiling acetonitrile and filtered while hot to give 0.60 g (66%) of **4a** as a green solid: m.p. 273–274°; IR ν_{max}^{KBr} cm^{-1}: 1590, 1490, 1440, 1230, 940, 850, 753, 690; UV $\lambda_{max}^{CH_2Cl_2}$ nm (log ε): 520 (4.64); MS: *m/z* 692 ($C_{34}H_{24}{}^{130}Te_2$). Anal.: calc. for $C_{34}H_{24}Te_2$: C, 59.4; H, 3.5%; found: C, 59.4; H, 3.3%.

Preparation of $\Delta^{4,4'}$*-2,2',6,6'-tetra-t-butyl-4-(tellurapyranyl)-4H-tellurapyran* (**4b**). Thione (**10b**) (1.35 g, 4.02 mmol) and copper powder (1.25 g) slurried in 20 ml of toluene were heated under reflux for 16 hr. The reaction mixture was filtered while hot through a pad of Celite and the pad was washed with CH_2Cl_2 (2 × 50 ml). The combined organics were concentrated and the residue was recrystallized from MeCN to give 0.98 g (80%) of **4b**: m.p. 273–275°; IR ν_{max}^{KBr} cm^{-1}: 2970, 1620, 1475, 1466, 1458, 1364, 1231, 1031, 950, 848, 810; UV $\lambda_{max}^{CH_2Cl_2}$ nm (log ε): 435 (4.69); FDMS: *m/z* 612 ($C_{26}H_{40}{}^{130}Te_2$). Anal.: calc. for $C_{26}H_{40}Te_2$: C, 51.4; H, 6.6; Te, 42.0%; found: C, 51.1; H, 6.8; Te, 40.3%.

Preparation of $\Delta^{4,4'}$*-2,2',6,6'-tetramethyl-4-(tellurapyranyl)-4H-telluropyran* (**4c**). Thione (**10c**) (0.50 g, 2.0 mmol) and copper powder (1.0 g) were slurried in 10 ml of toluene. The mixture was warmed under reflux for 2.5 hr and filtered through a 5 cm pad of alumina (activity II) in a 5 cm I.D. column. The pad was eluted with 200 ml of CH_2Cl_2. The combined organic filtrates were concentrated. The residue was boiled in acetonitrile, cooled, and filtered to give 0.14 g (32%) of **4a** as a yellow solid: m.p. 212–217° (dec); ^{1}H-NMR ($CDCl_3$): δ 6.73 (s, 4H), 2.27 (s, 12H); IR ν_{max}^{KBr} cm^{-1}: 2900, 1615, 1420, 1310, 1115, 1080, 900, 842; MS: *m/z* 444 ($C_{14}H_{16}{}^{130}Te_2$). Anal.: calc. for $C_{14}H_{16}Te_2$: C, 38.3; H, 3.7; Te, 58.1%; found: C, 38.6; H, 3.7; Te, 58.2%.

Preparation of $\Delta^{4,4'}$*-2,2',6,6'-tetraphenyl-4-selenapyranyl)-4H-selenapyran* (**3a**). Thione (**9a**) (3.27 g, 0.0100 mol) and copper powder (3.0 g) slurried in 30 ml of toluene were heated at reflux under N_2 for 16 hr. The mixture was filtered through a pad of Celite while hot. The Celite pad was washed with CH_2Cl_2 (3 × 50 ml), and the combined organics were concentrated. The residue was digested with 100 ml of boiling acetonitrile. After the acetonitrile had cooled to ambient temp, crystalline **3a** was filtered from soln to give 1.92 g (65%) of material: m.p. 297–299° (lit.[2] m.p. 299–302°); UV $\lambda_{max}^{CH_2Cl_2}$ nm (log ε): 490 (4.62). Anal.: calc. for $C_{34}H_{24}Se_2$: C, 69.2; H, 4.1; Se, 26.7%; found: C, 69.1; H, 4.1; Se, 27.0%.

Preparation of $\Delta^{4,4'}$*-2,2',6,6'-tetra-t-butyl-4-(selenapyranyl)-4H-selenapyran* (**3b**). Thione (**9b**) (3.10 g, 10.8 mmol) and copper powder (2 g) slurried in 25 ml of xylenes were heated at reflux for 24 hr. The mixture was filtered while hot through Celite. The filter cake was washed with CH_2Cl_2 (3 × 50 ml) and the combined organics were concentrated. The residue was recrystallized from acetonitrile to give 1.40 g (51%) of **3b**: m.p. 260–263; FDMS: *m/z* 512 ($C_{26}H_{40}{}^{80}Se_2$). Anal.: calc. for $C_{26}H_{40}Se_2$: C, 61.2; H, 7.9%; found: C, 61.2; H, 7.7%.

Preparation of $\Delta^{4,4'}$*-2,2',6,6'-tetramethyl-4-(selenapyranyl)-4H-selenapyran* (**3c**). Thione (**9c**) (1.00 g, 4.92 mmol) and copper powder (1.0 g) slurried in 25 ml of toluene were heated at reflux for 16 hr under N_2. The mixture was filtered through Celite while hot. The Celite pad was washed with CH_2Cl_2 (2 × 50 ml) and the combined organics were concentrated. The residue was stirred with 50 ml of boiling acetonitrile. Upon cooling, crystalline **3a** was collected by filtration to give 0.38 g (45%): m.p. 210–212° (lit.[2] m.p. 180°); FDMS: *m/z* 344 ($C_{14}H_{16}{}^{80}Se_2$). Anal.: calc. for $C_{14}H_{16}Se_2$: C, 49.1; H, 4.7%; found: C, 49.0; H, 4.7%.

Preparation of $\Delta^{4,4'}$*-2,2',6,6'-tetra-t-butyl-4-(thiapyranyl)-4H-thiapyran* (**2b**). Thione (**8b**) (0.48 g, 2.0 mmol) and copper powder (1.5 g) slurried in 25 ml of xylene were heated at reflux for 24 hr. The reaction mixture was filtered while hot through Celite and the Celite pad was washed with 25 ml of hot xylene. The combined organics were concentrated and the residue was treated with 50 ml of boiling acetonitrile. Upon cooling, crystalline **2b** was collected to give 0.17 g (39%): m.p. 257–258°; FDMS: *m/z* 416 ($C_{26}H_{40}S_2$). Anal.: calc. for $C_{26}H_{40}S_2$: C, 74.9; H, 9.7%; found: C, 74.7; H, 9.8%.

Preparation of ^{125}Te, ^{125}Te-$\Delta^{4,4'}$*-2,2'6,6'-tetra-t-butyltellurapyranyltellurapyran.* A 96% enriched sample of ^{125}Te (Oakridge National Laboratory) (0.19 g, 1.5 mmol) was added to 3 ml of 1 M lithium triethylborohydride in tetrahydrofuran (THF). The mixture was stirred for 2 hr under Ar and diluted with 5 ml of 1 M NaOEt in EtOH. 2,2,8,8-Tetramethyl-3,6-nonadiyn-5-one (0.35 g, 1.8 mmol) in 5 ml of 1 M NaOEt in EtOH was added. The mixture was stirred for 30 min at ambient temp and diluted with H_2O (65 ml). The products were extracted with CH_2Cl_2 (3 × 25 ml). The combined organic extracts were dried over $MgSO_4$, filtered through Celite and concentrated. Chromatography of the residue on silica gel eluted with 10% MeOH in CH_2Cl_2 gave 0.17 g (35%) of the ^{125}Te-2,6-di-*t*-butyltellurapyranone. ^{1}H-NMR ($CDCl_3$): δ 6.97 (d, 2H, J = 5.4 Hz), 1.31 (d, 18H, J = 3.7 Hz); FDMS: *m/z* 317 ($C_{13}H_{20}O^{125}Te$).

The ^{125}Te-tellurapyranone (0.16 g, 0.50 mmol) was dissolved in 2 ml of toluene. Lawesson reagent (0.20 g) was added and the mixture was heated at reflux for 10 min. Copper powder (0.20 g) was added. The mixture was cooled to room temp and filtered through a 5 cm pad of alumina in a 2 cm diameter column eluted with CH_2Cl_2. The filtrate was concentrated and the residue was recrystallized from MeCN to give 0.10 g (67%) of the yellow dimer: m.p. 273–275°; FDMS: *m/z* 602 ($C_{26}H_{40}{}^{125}Te_2$).

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