under argon for 3 days. The resulting mixture was chromatographed as described above, and 0.12 g (0.60 mmol; 69%) of *N*-(4-chloro-2-nitrophenyl)ethylamine (**9**) was isolated: MS (57), 185 (100); for NMR see Table II; mp 90.5 °C (lit.[26] mp 93 °C). In another experiment **8** was heated with acetic acid, water, and sodium nitrite in molar ratios corresponding to the nitrosation of 2 h. Chromatography permitted the isolation of a small amount of **9**. The presence of **9** in the original nitrosation mixture (after 2 h) of **4** was demonstrated by HPLC coinjection of **9**.

Nitrosation of *N*-(4-Chlorophenyl)dibenzylamine (3). *N*-(4-Chlorophenyl)dibenzylamine was nitrosated as described for **4**. HPLC analysis showed the reaction mixture to contain (4-chlorophenyl)benzylnitrosamine (**5**) (99%) as the sole product derived from **4**. Workup gave **5**, which was recrystallized from hexane: mp 55 °C (lit.[27] mp 57 °C); for NMR see Table II.

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Registry No. **1**, 4280-30-2; **2**, 41173-36-8; **3**, 15429-21-7; **4**, 2873-89-4; **6**, 1008-93-1; **7**, 86309-90-2; **8**, 86309-91-3.

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[26] Behrens, M. H. *Recl. Trav. Chim. Pays-Bas* **1901**, *21*, 274.

[27] Carter, P.; Stevens, T. *J. Chem. Soc.* **1961**, 1743.

New Donors with Two-Electron Oxidation. Synthesis and Electrochemical Properties of Highly Conjugated Bis(4*H*-pyrans), Bis(4*H*-thiopyrans), and Bis(flavenes)

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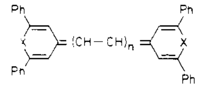
Highly conjugated $\Delta^{4,4'}$-bis(4*H*-pyrans), -(4*H*-thiopyrans), and -(flavenes) separated by four and six ethanediylidene groups were synthesized by condensing the bis Wittig–Horner reagent of tetraethyl 2-butene-1,4-diyldiphosphonate with the appropriate aldehydes. The bispyran separated by three ethanediylidene groups was prepared from the vinylogous pyranyl Peterson reagent generated in situ from 2,6-diphenyl-4-[(trimethylsilyl)ethenyl]-4*H*-pyran, which was synthesized from the corresponding acetylenic derivative by selective hydrogenation. The cyclic voltammograms of these highly conjugated donors are compared with those of the simple derivatives that are separated only by zero to two ethanediylidene groups. The two single-electron waves that are characteristic of the latter coalesce to one *two-electron* oxidation wave when the number of carbons in the extended conjugation separating the two pyranyl, thiopyranyl, and flavenyl moieties reaches eight. One of the extended bisthiopyrans studied, upon one-electron electrochemical oxidation, produces a 50:50 mixture of the neutral and the dicationic species in the presence of <10% of the cation radical species in methylene chloride.

Donors having *two* one-electron, reversible cyclic voltammetric oxidations are quite common.[1] The optimal peak potentials of the first wave for donors to form conducting mixed-valence charge-transfer complexes are believed to fall between $E^{\circ\prime} = 0$ and +0.4 V (vs. SCE).[2] Donor molecules with the unique electrochemical property of *one two-electron reversible* oxidation in this range, nevertheless, are extremely rare.[3] We are intrigued by the possibility that such a molecule D^0, once properly oxidized with a suitable acceptor A^0, might give rise to the kind of mixed-valence CT complexes (such as $D^0D^{2+} \cdot A_2^-$) that are conducive to a two-electron transport process through the molecular stack.

After our earlier studies of the synthesis and electrochemical properties of certain polyene-separated bispyrans and bisthiopyrans,[4,5] we noted that, by systematically extending the conjugation separating the two pyran and thiopyran moieties in **1**, we were able to make the two one-electron, reversible oxidation waves coalesce to a single two-electron redox couple.[5] For example, the simple phenyl-substituted bisthiopyran **1** (X = S, n = 0) has $E_{\mathrm{I}}^{\circ\prime}$ = +0.27 V and $E_{\mathrm{II}}^{\circ\prime}$ = +0.48 V, with a separation of 210 mV, whereas the diethynylidenyl derivative **1** (X = S, n = 2) has $E_{\mathrm{I}}^{\circ\prime}$ = +0.21 V and $E_{\mathrm{II}}^{\circ\prime}$ = +0.34 V, with a separation of half-wave potentials of 130 mV (see Table II). We attributed this interesting phenomenon to the gradual decrease in energy in removing the second electron from the radical cation of **1**, because the dication **2** that is produced encounters less coulombic repulsion as the length of the conjugation separating the pyrylium or thiopyrylium functions increases. We envisaged that, by extending this conjugation *further* (i.e., $n > 2$), it should be possible to bring the two one-electron oxidation waves of **1** together



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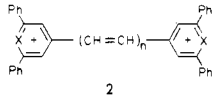

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[1] Chen, C. H.; Reynolds, G. A. *J. Org. Chem.* **1980**, *45*, 2449. Chambers, J. Q.; Moses, P. R. *J. Am. Chem. Soc.* **1974**, *96*, 945. Engler, E. M.; Kaufman, F. B.; Green, D. C.; Compton, R. N.; Klots, C. E. *Ibid.* **1975**, *97*, 2921. Narita, M.; Pittman, C. U., Jr. *Synthesis* **1976**, 489. Perlstein, J. H. *Angew, Chem., Int. Ed. Engl.* **1977**, *16*, 519. Scott, B. A.; Kaufman, F. B.; Engler, E. M. *J. Am. Chem. Soc.* **1976**, *98*, 4342. Wudl, F.; Schafer, D. E.; Miller, B. *Ibid.* **1976**, *98*, 252. Hünig, S.; Ruider, G. *Justus Liebigs Ann. Chem.* **1974**, 1415.

[2] Torrance, J. B. *Acc. Chem. Res.* **1979**, *12*, 79.

[3] Chen, C. H.; Reynolds, G. A. *J. Org. Chem.* **1981**, *45*, 2449. Bard, A. J.; Phelps, J. *J. Electronal. Chem.* **1970**, *25*, App 2; **1976**, *68*, 313. Hünig, S.; Ruider, G. *Liebigs Ann. Chem.* **1974**, 1415.

[4] Reynolds, G. A.; Chen, C. H. *J. Org. Chem.* **1981**, *46*, 184.

[5] Reynolds, G. A.; Chen, C. H. *J. Heterocycl. Chem.* **1981**, *18*, 627.

0022-3263/83/1948-2757$01.50/0

Table I. Synthesis and Characterization of 1 and 6

starting aldehyde	m	X	product	n	formula[a]	mp, °C	M^{+}[b]	yield, %
4	0	O	1	3	$C_{40}H_{30}O_2$[c]	263-265	542	58
4	0	O	1	4	$C_{42}H_{32}O_2$[d]	279-280	568	18
4	0	S	1	4	$C_{42}H_{32}S_2$.	234-235	600	20
4	1	S	1	6	$C_{46}H_{36}S_2$	225-226	652	21
			6	2	$C_{34}H_{24}O_2$	278-279	464	80
5	0		6	4	$C_{38}H_{28}O_2$	278-279	516	27
5	1		6	6	$C_{42}H_{32}O_2$	170-171	568	17

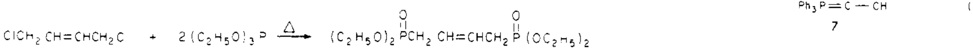
[a] Satisfactory combustion analytical data were provided for these compounds, C, H (±0.4%). [b] Field-desorption mass spectra (m/e). [c] C, H, O (calcd 88.5, 5.6, 5.9; found 86.7, 5.5, 6.0). [d] C, H (calcd 88.7, 5.6; found 88.1, 5.4).

so that they would be expected to coalesce to form one two-electron redox couple.

This paper describes the synthesis and the electrochemical properties of several highly conjugated $\Delta^{4,4'}$-bis-(4*H*-pyrans), -(4*H*-thiopyrans), and -(flavenes) with the desired *two-electron, reversible* oxidations within the range of $E^{\circ\prime}$ of 0 to +0.4 V (vs. SCE) in their cyclic voltammograms. The extended bisthiopyran donor 1 (X = S, n = 4), upon *one-electron* electrochemical oxidation, produces a 50:50 mixture of the neutral D^0 and the dicationic D^{++} species plus small quantities of the cation radical ($D^{+\cdot}$) species.

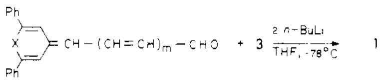
Results

Synthesis of 1 and Flavene 6 with n = 4 and 6. The most efficient synthesis of dimers 1 and 6 with n = 4 and 6 is, we believe, similar to the one described in the convergent synthesis of vitamin A with the bis Wittig–Horner reagent 3.[6] The latter can be readily prepared in 58% yield by heating a mixture of *trans*-1,4-dichloro-2-butene and 2 equiv of triethyl phosphite at ca. 150 °C under the Arbuzov conditions. The same reaction with *trans*-1,4-dibromo-2-butene, interestingly, does not work. The Wittig–Horner reagent of tetraethyl 2-butene-1,4-diyldiphosphonate (3), which serves as the source for two conjugated ethylene units, can be condensed with 2 equiv of a variety of extended pyranyl, thiopyranyl, and flavenyl aldehydes 4 and 5 to give 1 and 6, respectively. The experimental conditions used for these reactions were similar to those described for the preparation of the 4,4′-(ethanediylidene)bis(4*H*-pyran) derivatives 1 (X = O, n = 1)[4] except that 1 equiv of BuLi and the corresponding aldehyde were added consecutively to 3 cooled at −78 °C in THF, and then an additional equivalent of each of these reagents was added. All of these products are very dark crystalline solids with very high melting points (with decomposition), soluble in nonpolar solvents such as methylene chloride and benzene, and sparingly soluble in polar solvents such as acetonitrile. Above all, they are remarkably stable in air. Because their IR and ^{1}H NMR spectra do not provide much useful information, characterizations of these compounds relied mostly on field-desorption mass spectrometry and elemental combustion analyses. The results are tabulated in Table I. All the starting aldehydes are known compounds, prepared from the corresponding active-methyl compound and (diethylamino)acrolein followed by hydrolysis.[7]



$ClCH_2CH{=}CHCH_2Cl + 2(C_2H_5O)_3P \xrightarrow{\Delta} (C_2H_5O)_2\overset{O}{\overset{\|}{P}}CH_2CH{=}CHCH_2\overset{O}{\overset{\|}{P}}(OC_2H_5)_2$

3



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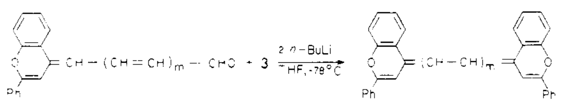
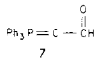


5 6

Theoretically, this method can be exploited to synthesize even higher vinylogues of 1 (e.g., n = 8, 10), provided that the appropriate higher vinylogues of aldehydes 4 can be readily prepared. We have explored the possibility of a two-carbon extension of 4 by using the Wittig reagent 7[8] and the masked Wittig-Horner reagent 8.[9] Only the more reactive reagent 8 condensed with 4 to give the desired imino derivative 9, which was hydrolyzed to give the extended aldehyde 10. The yields of 9, however, were somewhat lower than expected, and this chemistry was not pursued further.



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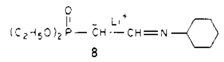

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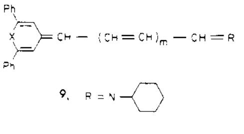
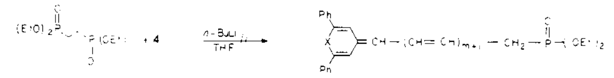


10, R = O

Synthesis of 1 with n = 3. Because the diphosphonate 3 would not allow access to 1 with n = 3, a new method was sought. Our first goal was to prepare the extended pyranyl and thiopyranyl phosphonates 12 by the reaction of the Wittig–Horner reagent of 11[10] with 1 equiv of aldehyde 4, because 12 would allow us to synthesize *un-symmetrical* 1 that could not otherwise be obtained by use of the bis Wittig–Horner reagent 3. Unfortunately, this reaction could not be controlled to yield either 12 or 1 selectively. ^{1}H NMR suggested the formation of 12, but mass spectral analysis of the crude product 12 showed further condensation of 12 with 4. Other attempts to synthesize the *extended* thiopyranyl phosphonate 16 starting from the readily available 4-ethylthiopyrylium perchlorate 13 by successive treatment with 2 equiv of LDA, or 1 equiv of LDA and then 2 equiv of *n*-BuLi/



11 12

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(6) Pommer, H. *Angew. Chem.* **1960**, *72*, 911.

(7) Reynolds, G. A.; Van Allan, J. A. *J. Org. Chem.* **1969**, *34*, 2736.

(8) Snyder, J. P.; Bestmann, H. J. *Tetrahedron Lett.* **1970**, 3317.

(9) Hagata, W.; Hayase, Y. *Tetrahedron Lett.* **1968**, 4359.

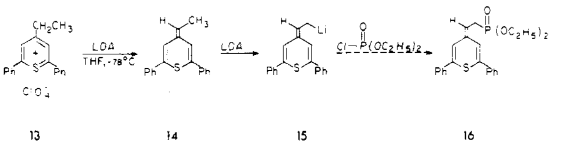
(10) Masdritzer, K.; Irain, R. R. *J. Inorg. Nucl. Chem.* **1961**, *22*, 297.

Table II. Electrochemical Properties of Polyene-Separated $\Delta^{4,4'}$-Bis(4*H*-pyrans), -(thiopyrans), and -(flavenes)

			wave I,[a] V		Δ(Ep anodic − Ep cathodic)	wave II,[a] V		Δ(Ep anodic − Ep cathodic)	ΔV,[b] V
structure	X	*n*	Ep anodic	Ep cathodic		Ep anodic	Ep cathodic		
1	O	0	+0.17	+0.11	0.060	+0.49	+0.43	0.060	+0.32
	S	0	0.31	0.24	0.070	0.52	0.45	0.070	0.21
6		0	0.41	0.36	0.070	0.55	0.49	0.060	0.13
1	O	1	0.13	0.06	0.070	0.47	0.41	0.060	0.34
	S	1	0.22	0.16	0.060	0.47	0.41	0.060	0.24
6		1	0.41	0.36	0.070	0.63	0.57	0.060	0.22
1	O	2	0.22	0.16	0.060	0.42	0.36	0.060	0.20
	S	2	0.24	0.18	0.060	0.37	0.31	0.060	0.13
6		2	0.34	0.28	0.060	0.53	0.47	0.060	0.20
1	O	3	0.18	0.11	0.070	0.29	0.21	0.080	0.10
1	O	4	0.19	0.15 (2e)	0.040				
	S	4	0.23	0.19 (2e)	0.040				
6		4	0.37	0.32 (2e)	0.050				
1	S	6	0.22	0.17 (2e)	0.050				
6		6	0.29	0.26 (2e)	0.030				

[a] Solvent, CH_2Cl_2; supporting electrolyte, 0.1 M TBAF; indicating electrode, glassy carbon; reference electrode, SCE; sample concentration, $< 5 \times 10^{-4}$ M; scan rate, 0.1 V/s. [b] Difference in potential midpoints between forward and reverse peaks of the two one-electron reversible waves.

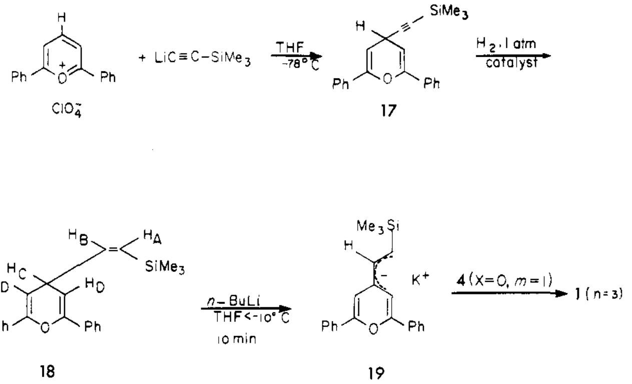
HMPA, followed by trapping of the lithiated anion **15** with diethyl chlorophosphate were also unsuccessful. Presumably, the "methylene" compound **14** generated in situ was not efficiently deprotonated by LDA or *n*-BuLi/HMPA under the experimental conditions. *n*-BuLi added to the thiopyrylium **13** at the 4-position instead of causing deprotonation, as shown by mass spectrometry (*m*/*e* 334, M^+ for $C_{23}H_{26}S$).



Scheme I shows our successful approach toward the synthesis of the vinylogue of a Peterson reagent of 2,6-diphenyl-4-(trimethylsilyl)-4*H*-pyran. The 4-(trimethylsilyl)acetylenic 4*H*-pyran **17** was prepared in 99% yield by addition of the lithiated (trimethylsilyl)acetylene to the pyrylium perchlorate.[11] Selective hydrogenation of **17** with poisoned catalyst, Pd/$BaSO_4$ and quinoline,[12] at room temperature gave the *cis*-[(trimethylsilyl)vinyl]pyran **18** in 70% yield. The stereochemistry of the double bond in **18** is supported by its ^{1}H NMR spectrum, which has a large cis coupling J_{AB} = 13 Hz. Compound **18** was metalated with *n*-BuLi in THF at <−10 °C under argon; a dark green solution of the metalated species formed instantly. Because the 4*H*-pyranyl anion is antiaromatic,[13] the charge density presumably is localized at the carbon α to the silicon, which is known to stabilize an adjacent carbanion by d-orbital participation.[14] Hence, we have, in essence, generated in situ the desired Peterson reagent **19**,[15] which can be readily condensed with the appropriate electrophiles **4** (X = O) to give the extended bispyran **1** (X = O) with *n* = 3. The results are included in Table I.

Electrochemical Properties of 1 and 6. The cyclic voltammetric data of the highly conjugated **1** and **6** prepared in this work are compared with those of the simple $\Delta^{4,4'}$-bis(4*H*-pyrans), -(thiopyrans), and -(flavenes) in Table II. The data are mostly self-explanatory. The two single-electron waves that are characteristic of the simple derivatives of bispyrans and bisthiopyrans[5] coalesce to one two-electron oxidation wave when the number of carbons in the extended conjugation separating the two pyranyl or thiopyranyl moieties reaches eight (i.e., **1**, *n* = 4). Typical examples of this coalescence phenomenon are demonstrated in Figure 1, which compares the cyclic voltammograms of the bisthiopyran **1** with *n* = 1 and *n* = 4. Further extension (e.g., *n* = 6) resulted in little change in the cyclic voltammogram. The bisflavenyl series behaves similarly. The midwave potentials of these "highly conjugated" donors fall well within the range between 0 and +0.4 V, where highly conducting mixed-valence charge-transfer salts are known to form.[2] From a synthetic point of view, among donors with the desired cyclic voltammetric properties, **1** (X = S) and **6** with *n* = 4 appear to be most attractive because their corresponding extended aldehydes **4** and **5** (*m* = 0) are relatively easy to prepare in high yield.

Scheme I



Electrochemical one-electron oxidation of the bisthiopyran **20** in methylene chloride (8.57×10^{-5} M) in the presence of tetrabutylammonium tetrafluoroborate (TBAF; 0.1 N) produced a dark red solution. The UV-visible spectra of this mixture and of the neutral donor **20** and the dication **21** are reproduced in Figure 2. The dication **21** can be independently prepared in methylene chloride solution under similar conditions by a stoichiometric two-electron electrochemical oxidation.

The one-electron oxidation of **20** by constant-potential electrolysis[16] gave $\dot{20}$ [λ_{max} 578 nm (ε 93 900)] and **21** [λ_{max}

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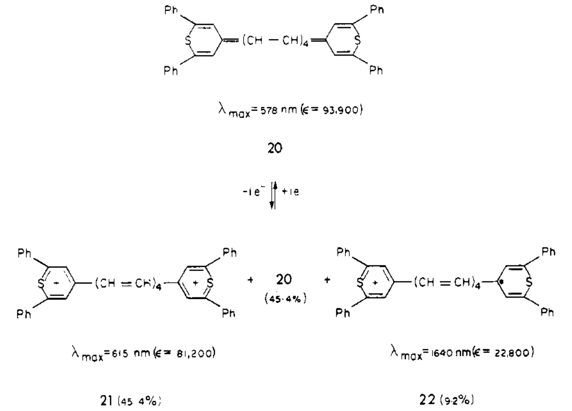
[11] Doney, J. J.; Chen, C. H, unpublished, results.

[12] Augustine, R. L. "Catalytic Hydrogenations"; Marcel Dekker: New York, 1965; pp 69–152. Zweifel, G. *Synthesis* **1980**, *10*, 803.

[13] Schmidt, R. R.; Burkert, U. *Tetrahedron Lett.* **1973**, 4355.

[14] Covin, E. W. *Chem. Soc. Rev.* **1978**, *7*, 15.

[15] Peterson, D. J. *J. Org. Chem.* **1968**, *33*, 780.



615 nm (ε 81 200)] in equal amounts comprising 91% of the total mixture. The cation radical species **22** [λ_{max} 1640 nm (ε 22 800)] made up the remaining 9% of the electrolysis mixture. We determined the concentration of the cation radical species (**22**) indirectly by using the known molecular absorptivities of the neutral (**20**) and dication (**21**) species to produce simulated spectra. The one-electron oxidation of **20** by constant-potential electrolysis[16] at +0.30 V (vs. SCE) provided an electronic spectrum that corresponded most closely to a simulated spectrum of a 1:1 mixture of **20** and **21** comprising 91% of the total mixture. The remaining 9% was attributed to the cation radical species **22**, whose presence is indicated by its electronic transitions in the infrared.[3] The concentrations of **20** and **21** could also be determined at a wavelength at which **22** absorbs negligibly in the visible, with the simulated spectra used to indicate these spectral regions. The relative amount of the cation radical species is extremely solvent dependent, and its concentration decreases drastically as the solvent polarity increases. In the 250–700-nm spectral region (see Figure 2) there appear to be five well-defined isosbestic points accompanying the transformation of **20** to **21**. This is presumably due to the fact that the cation radical species is present in low concentration. The presence of the cation radical species **22** in the one-electron oxidized solution suggests that oxidation at large separation appears to involve coupled centers[17,18] rather than noninteracting[19] centers as would be expected.

Experimental Section

Melting points were determined with a Thomas-Hoover capillary melting point apparatus. Field-desorption mass spectra were recorded on an MAT-731 mass spectrometer. Cyclic voltammograms were obtained on a Heath polarography system EUW-401. Microanalyses were performed by the Analytical Sciences Division, Kodak Research Laboratories. ^{1}H and ^{13}C NMR spectra were recorded on Varian EM-390 and CFT-20 spectrometers with Me_4Si as the internal standard. IR spectra were obtained on a Beckman IR-4250 spectrophotometer.

$\Delta^{4,4'}$-Bis(4*H*-thiopyran) 1 (X = S, *n* = 4). This experiment illustrates the general procedure used to synthesize 1 (X = O, S) and 6 with *n* = 4 and 6. To a solution of 2.26 g (6.89 mmol) of the diphosphonate 3[6] in 150 mL of dry THF was added by syringe 3.6 mL (1.1 equiv) of *n*-BuLi (2.1 M in hexane) at −78 °C under argon. To the resulting yellowish Wittig–Horner reagent was added dropwise through a graduated addition funnel approximately half of a solution of 4 g (2 equiv) of 4-(formylmethylene)-2,6-diphenyl-4*H*-thiopyran 4 (X = S, *m* = 0)[7] in 160 mL of dry THF. The reaction mixture, which immediately turned dark green, was stirred at −78 °C for 10 min before 1 equiv (3.6 mL) of *n*-BuLi was added by syringe. The dark green reaction mixture, which had thickened considerably, was stirred at −78 °C for 10 min, and then the rest of 4 in the addition funnel was added dropwise. The very dark mixture was allowed to equilibrate to room temperature overnight and poured into a beaker containing ca. 1.3 L of water. The mixture was stirred in a well-ventilated hood for ca. 4 h to allow some of the excess THF to evaporate. The precipitated dark solid was then filtered, washed with water, and air-dried to give 3.1 g of the crude bisthiopyran 1 (X = S, *n* = 4), which was purified by recrystallization from 100 mL of toluene to give 660 mg (16%) of the pure crystalline material.

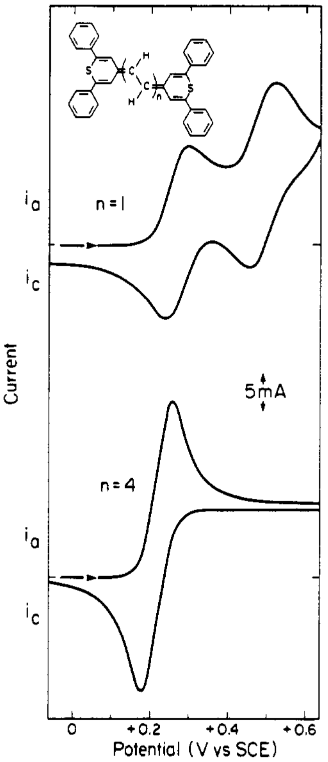


Figure 1. Cyclic voltammogram of the bisthiopyran 1 with *n* = 1 and *n* = 4 in methylene chloride solvent containing 0.1 M tetrabutylammonium tetrafluoroborate as electrolyte. A platinum inlay electrode was made as the working electrode, and the scan rate was 100 mV/s. Concentration of 1 was 5.0 × 10^{-4} M.

Characterization of this and other compounds is presented in Table I.

2,6-Diphenyl-4-[(trimethylsilyl)acetenyl]-4*H*-pyran (17). To a stirred solution of 2.95 g of (trimethylsilyl)acetylene in 50 mL of dry ether at −77 °C under argon was added 14.3 mL of *n*-BuLi (2.1 M in hexane) dropwise by syringe. The lithiated acetylene was stirred for 15 min and then slowly transferred via a transfer needle with argon pressure into a stirred suspension of 10.0 g of 2,6-diphenylpyrylium perchlorate in 75 mL of dry ether at −77 °C under argon. The reaction mixture was allowed to warm to room temperature and stirred for 1 h; the reaction was followed by TLC on silica gel with 9:1 hexane/ethyl acetate. The solvent was removed on a rotary evaporator, while the reaction products were kept in an inert atmosphere. To the solid was added 150 mL of pH 7 aqueous phosphate buffer. The solid was then filtered and air-dried. If necessary, this material was eluted with hexane (if the product was exposed to air or moisture before the pH 7 wash, a dark green polar decomposition product formed). The product was stored under argon in a freezer. The reaction yielded 9.9 g (99%) of **17**: mp 91–93 °C; IR 2165 (C≡C) cm^{-1}; ^{1}H NMR

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[16] A Princeton Applied Research Model 173 potentiostat and Model 175 universal programmer were used in the standard three-electrode configuration to obtain the oxidation potentials of 1 by cyclic voltammetry. A platinum inlay electrode was used as the working electrode along with a platinum auxiliary electrode and a fiber standard calomel electrode. The electrolyte was 0.1 M tetrabutylammonium tetrafluoroborate (TBAF). A Princeton Applied Research Model 179 digital coulometer was used for coulometry experiments.

[17] Neta, P.; Evans, D. H. *J. Am. Chem. Soc.* **1981**, *103*, 7041.

[18] Olsen, B. A.; Evans, D. H. *J. Am. Chem. Soc.* **1981**, *103*, 839.

[19] Flannagan, J. B; Margel, S.; Bard, A. J.; Anson, F. C. *J. Am. Chem. Soc.* **1978**, *100*, 4248.

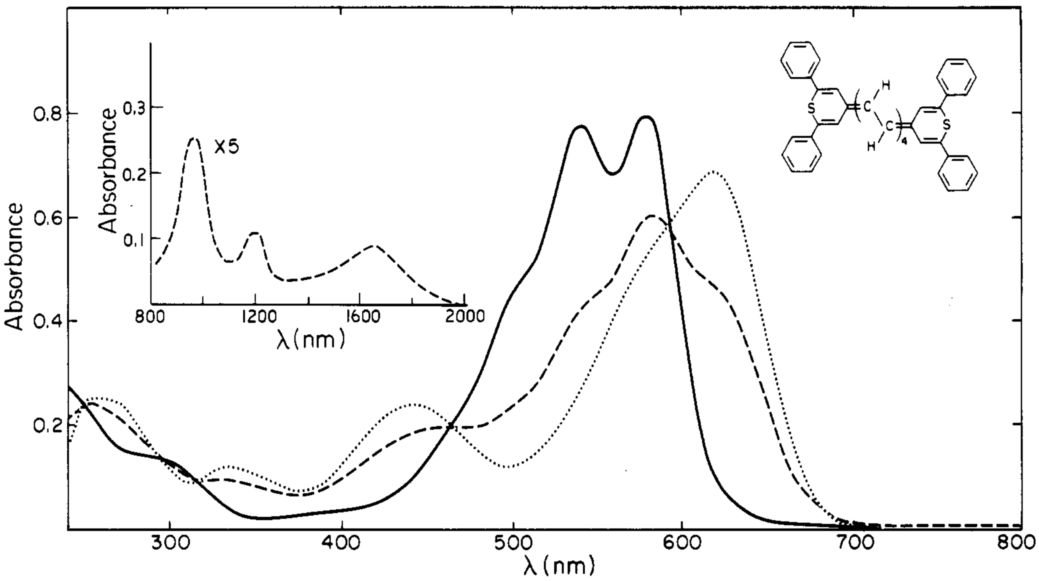

Figure 2. Absorption spectrum of the bisthiopyran 1 with $n = 4$ in methylene chloride, neutral (–), dication (···), and one-electron oxidation (- - -).

($CDCl_3$) δ 0.20 (s, 9), 4.23 (t, 1, $J_{XA} = 3.5$ Hz), 5.41 (d, 2, $J_{AX} = 3.5$ Hz), 7.35 (m, 6, *m*- and *p*-Ph H), 7.67 (m, 4, *o*-Ph H); ^{13}C NMR ($CDCl_3$) δ 148.5 (C-2), 96.4 (C-3), 25.3 (C-4), 107.8 ($C\equiv C$), 84.1 ($C\equiv CSi$), 0.0 ($SiCH_3$), 133.9, 128.5, 128.1, 124.5; mass spectrum, *m/e* 330 [M^+].

Anal. Calcd for $C_{22}H_{32}OSi$: C, 80.0; H, 6.7. Found: C, 80.4; H, 6.9.

2,6-Diphenyl-4-[(trimethylsilyl)ethenyl]-4*H*-pyran (18). To a solution of 9.9 g of 17 was added 800 mg of 5% $Pd/BaSO_4$ and 10 drops of reagent-grade quinoline. The reaction flask was connected to an atmospheric hydrogenation apparatus and stirred vigorously at room temperature under 1.05 atm of hydrogen pressure until 700 mL (1.1 equiv) of H_2 gas was consumed (~75 min). The reaction mixture was poured through Celite, and the solvent was removed on a rotary evaporator at ambient temperature. After chromatography on silica gel eluted with hexane, a yellow oil was obtained, which solidified overnight under high vacuum. The reaction yielded 7.0 g (70%) of 18: mp 85–87 °C; mass spectrum, *m/e* 332 (M^+).

Anal. Calcd for $C_{22}H_{24}OSi$: C, 79.6; H, 7.3. Found: C, 79.9; H, 7.3.

This material was used directly in subsequent reactions. Characterization of the yellow solid showed the following: ^1H NMR ($CDCl_3$) δ 0.22 (s, 9), 3.98 (dt, 1, H_C, $J_{DC} = 4$ Hz, $J_{BC} = 10$ Hz), 5.30 (d, 2, H_D, $J_{CD} = 4$ Hz), 5.52 (d, 1, H_A, $J_{BA} = 13$ Hz), 6.28 (dd, 1, H_B, $J_{AB} = 13$ Hz, $J_{CB} = 10$ Hz), 7.35 (m, 6, *m*- and *p*-Ph H), 7.67 (m, 4, *o*-Ph H); ^{13}C NMR ($CDCl_3$) δ 148.6 (C-2), 99.2 (C-3), 36.7 (C-4), 151.2 ($CC=C$), 134.4, 128.2, 127.7, 124.5.

Synthesis of $\Delta^{4,4'}$-Bis(4*H*-pyran) 1 (X = O, *n* = 3) from the Peterson Reagent 19. To a stirred solution of 20 mL of dry THF, 5 mL of HMPA, and 660 mg of 18 (1.0 equiv) at a pot temperature of −10 °C (acetone/ice) was added dropwise 1.6 mL of *n*-BuLi (1.6 M in hexane). The red color associated with anion 19 was noted instantly. The reaction mixture was stirred for 10 min at <−10 °C, and 340 mg (1.1 equiv) of the aldehyde 4 (X = O, *m* = 1) in THF was added quickly. The mixture was allowed to warm to room temperature and refluxed for 30 min. The reaction mixture was poured into 400 mL of H_2O, stirred for 2 h, and filtered. The dark red solid was purified by refluxing in 20 mL of MeOH, filtering, refluxing in 20 mL of hexane, filtering, and drying at ambient temperature to yield 635 mg (58%) of 1 (X = O, *n* = 3): mp 263–265 °C; mass spectrum, *m/e* 542 (M^+ for $C_{40}H_{30}O_2$).

$\Delta^{4,4'}$-Bis(4*H*-flavene) 6 (*n* = 2). A suspension of 0.92 g (3 mmol) of flavylium perchlorate in 35 mL of dry THF was stirred under argon and chilled in a dry ice/acetone bath. A solution of 1.5 mL (3 mmol) of sodium diethylphosphonate (2 M in benzene) was added, and stirring was continued until a clear solution was obtained. To the solution was added 1.25 mL (3 mmol) of 2.4 M *n*-butyllithium (deep red); this solution was stirred for 5 min, and 0.82 g (3 mmol) of 4-(3-formyl-2-propen-1-ylidene)-2-phenyl-4*H*-flavene[7] was added. The mixture was stirred for 1 h in the cooling bath and then allowed to stand overnight at room temperature. The orange solid was collected and recrystallized from toluene, giving 0.56 g of product: mp 278–279 °C.