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Pyranylidenemethyl- and Thiopyranylidenemethyl-substituted Furans, Thiophenes, and *N*-Methylpyrroles as Precursors of Organic Metals and Third-order Nonlinear Optical Materials

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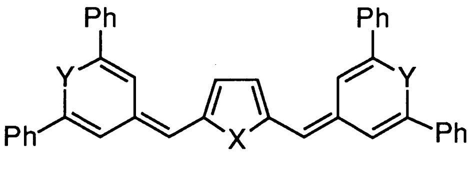
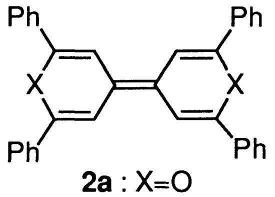
The title heteroaromatics have been synthesized by Wittig-Hornor reactions of the appropriate heterocyclic dialdehydes with diethyl pyranyl- and thiopyranyl-phosphonate. Cyclic voltammetry indicated their strong π-donor abilities, and some TCNQ complexes showed high electrical conductivities. They were also found to have large third-order nonlinear optical susceptibilities.

Recent attention in the field of organic metals has been directed towards the designs of extensively conjugated electron donors and acceptors.[1)] As a new class of such promising electron donors, we have been interested in bipyranylidene and bithiopyranylidene systems **1** with a heterocyclic spacer group, since parent bipyranylidene **2a** and bithiopyranylidene **2b** are strong electron donors and the incorporated heterocyclic rings serve not only to decrease intramolecular coulombic repulsion but also to enhance intermolecular interactions.[2)] In addition, such conjugated heteroaromatics as **1** are becoming of current interest in the development of organic materials showing nonlinear optical activities.[3)] Compared to extensive researches conducted on the development of new compounds with second-order nonlinearities, the study of third-order nonlinear optical materials has been relatively limited, and guidelines for molecular structural requirements for enhancing the third-order



1a : X=Y=O
1b : X=S, Y=O
1c : X=NMe, Y=O
1d : X=O, Y=S,
1e : X=Y=S
1f : X=NMe, Y=S



2a : X=O
2b : X=S

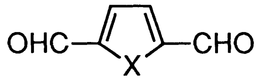
Table 1. Yields and properties of **1**

Compd	Yield/%	Appearance$^{a)}$	Dp/°C	MS(M^+)/*m*/*z*	$E_{1/2}(1)/V^{b)}$	$E_{1/2}(2)/V$	$\Delta E/V$
1a	76	reddish purple needles	221	556	0.16	0.30	0.14
1b	91	reddish purple needles	238	572	0.24	0.36	0.12
1c	48	reddish purple needles	245	569	0.03	0.25	0.22
1d	79	brown powder	214	588	0.25		0
1e	62	black crystals	193	604	0.32		0
1f	79	reddish purple needles	120	601	0.11	0.30	0.19

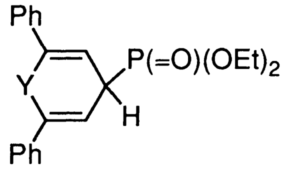
a) From benzene-hexane. b) vs. Ag/AgCl reference electrode in benzonitrile containing Bu_4NClO_4 as supporting electrolyte.

susceptibility have not been established yet.$^{4)}$ In this communication, we like to report on the synthesis, electrochemical properties, and third-order nonlinearities of **1**.

A series of the heteroaromatics **1** were synthesized by Wittig-Hornor reactions between the appropriate heteroaromatic dialdehydes **3**$^{5)}$ and the corresponding ylides which were generated in-situ from treatment of diethyl 2,6-diphenyl-*4H*-pyran-4-ylphosphonate **4a**$^{6)}$ and diethyl 2,6-diphenyl-*4H*-thiopyran-4-ylphosphonate **4b**$^{7)}$ with butyllithium in dry tetrahydrofuran (THF).$^{8)}$ The yields and properties of **1** are summarized in Table 1. All the compounds **1** are deeply colored with absorption maxima at around 500 nm.



3a : X=O
3b : X=S
3c : X=NMe



4a : X=O
4b : X=S

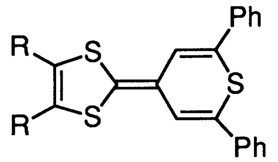
The oxidation potentials of **1** measured by cyclic voltammetry demonstrate strong π-donor abilities, which depend on the heterocyclic spacers; the first half-wave oxidation potentials decrease in the order of pyrrole, furan, and thiophene derivatives. The *N*-methyl pyrrole spacer thus contributes to a considerable increase in donor character, and as a result, **1c** and **1f** become stronger electron donors than **2a** ($E_{1/2}$ 0.12 and 0.49 V) and **2b** ($E_{1/2}$ 0.19 and 0.41 V), respectively. In addition, all the spacers cause a decrease in the difference between the first and second oxidation potentials, confirming marked reduction of intramolecular coulombic repulsion as expected. In particular, the introduction of the furan and thiophene spacers is very effective, as demonstrated by coalescence of the two peakes for **1d** and **1e**. A preliminary examination revealed that strong electron donors **1c** and **1f** could form 1:2 charge-transfer complexes with tetracyanoquinodimethane (TCNQ) and these complexes were highly conductive; **1c**•TCNQ 0.35 Scm^{-1} and **1f**•TCNQ 1.0 Scm^{-1}.

The third-order nonlinearities of **1** except **1d** with poor solubility were evaluated by the measurements of optical Kerr effects near the absorption edges of each compound in 1 wt/vol %

Table 2. Third-order nonlinear optical properties of **1**

Compd	$\chi^{(3)}/\times10^{-12}$ esu a)	λ_{max}(log ε)/nm b)	$\lambda_{meas.}$ /nm c)	α /cm^{-1} d)
1a	330	496.4 (4.56)	640.7	80
1b	300	500.8 (4.60)	640.7	100
1c	260	480.4 (4.71)	640.7	70
1d	—— e)	513.8 (4.59)		
1e	77	526.0 (4.66)	686.7	90
1f	280	501.0 (4.69)	658.7	55

a) Third-order nonlinear optical susceptibilities were measured with 1.0 wt/vol % solution in THF and converted to the values of 100%. A dye laser pumped with the third harmonics of a Q-switched Nd-YAG laser was used as a light source. The pulse duration was about 10 ns and the repetetion rate was 10 Hz. b) Absorptiom maxima measured in THF. c) Measurement wavelengths. d) Absorption coefficients at $\lambda_{meas.}$ converted to the values of 100 %. e) Not measured because of the poor solubility of **1d**.



5a : R=H
5b : R,R=SCH_2CH_2S

THF solution.9) The results are shown in Table 2, where the $\chi^{(3)}$ values of the sample solutions are calculated using that of carbon disulfide as the standard which was determined to be 1.0 x 10^{-12} esu, and converted to the values of 100 %. The observed susceptibilities are of the order of 10^{-10} esu, which are one or two orders of magnitude larger than those of various low-molecular compounds involving similar π-conjugated systems **5a** (30 × 10^{-12} esu) and **5b** (50 × 10^{-12} esu) previously screened by the same technique.9)

The present results indicate that pyranylidenemethyl- and thiopyranylidenemethyl-substituted furans, thiophenes, and *N*-methylpyrroles **1** have the potential not only as good electron donors for organic metals but also as promising candidates for third-order nonlinear optical materials.

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8) All the new compounds **1** were prepared according to the following general procedure. To a solution of diethyl 2,6-diphenyl-*4H*-thiopyran-4-ylphosphonate **4b** (1.05 g, 2.7 mmol) in dry THF (30 ml) was added butyllithium (1.5 *M* hexane solution, 1.8 ml, 2.7 mmol) under nitrogen atmosphere at -78 °C. After stirring for 15 min, a solution of *N*-methylpyrrole-2,5-dicarbaldehyde **3c** (150 mg, 1.09 mmol) in dry THF (10 ml) was slowly added, and the stirring was continued overnight while the temperature was allowed to rise to room temperature. The mixture was poured into aqueous saturated NH_4Cl solution and then extracted with dichloromethane. The extract was dried over anhydrous $MgSO_4$, passed through a short column of silica gel, and evaporated. Recrystallization of the resulting solid from hexane-benzene afforded reddish purple needles of **1f** (520 mg, 79%). All the compounds **1** gave satisfactory elemental analyses, and their ^{1}H NMR data ($CDCl_3$, 400 MHz) are as follows; **1a**: δ=5.71 (s, 2H, olefinic), 6.28 (d, J=1.8Hz, 2H, pyranic), 6.42 (s, 2H, furanic), 7.16 (d, J=1.8Hz, 2H, pyranic), 7.35-7.50 (m, 12H, Ph), 7.70 (dd, J=8.0, 1.0Hz, 4H, Ph), and 7.77 (dd, J=8.0, 1.0Hz, 4H, Ph); **1b**: δ=6.13 (s, 2H, olefinic), 6.43 (d, J=1.8Hz, 2H, pyranic), 6.88 (s, 2H, thiophenic), 7.22 (d, J=1.8Hz, 2H, pyranic), 7.35-7.48 (m, 12H, Ph), 7.76 (dd, J=7.3, 1.6Hz, 4H, Ph), and 7.74 (dd, J=7.3, 1.6Hz, 4H, Ph); **1c**: δ=3.55 (s, 3H, CH_3), 5.72 (s, 2H, olefinic), 6.43 (d, J=1.8Hz, 2H, pyranic), 6.51 (s, 2H, pyrrolic), 7.07 (d, J=1.8Hz, 2H, pyranic), 7.34-7.50 (m, 12H, Ph), 7.76 (d, J=7.4Hz, 4H, Ph), and 7.74 (d, J=7.4Hz, 4H, Ph); **1d**: δ=5.90 (s, 2H, olefinic), 6.37 (s, 2H, furanic), 6.71 (s, 2H, thiopyranic), 7.30-7.45 (m, 12H, Ph), 7.54-7.62 (m, 8H, Ph), and 7.76 (s, 2H, thiopyranic); **1e**: δ=6.37 (s, 2H, olefinic), 6.75 (s, 2H, thiopyranic), 6.94 (s, 2H, thiophenic), 7.20-7.46 (m, 12H, Ph), 7.53 (s, 2H, thiopyranic), and 7.57-7.65 (m, 8H, Ph); **1f**: δ=3.53 (s, 3H, CH_3), 5.94 (s, 2H, olefinic), 6.52 (s, 2H, pyrrolic), 6.74 (s, 2H, thiopyranic), 7.34-7.45 (m, 14H, thiopyranic and Ph), and 7.57-7.65 (m, 8H, Ph).

9) The measurements of third-order optical nonlinearities were carried out using an optical Kerr effect, and the detailed method was described in the following reference; K. Morita, T. Suehiro, Y. Yokoh, and H. Ashitaka, *J. Photopolym. Sci. Technol.*, **6**, 229 (1993).

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