Pergamon

Tetrahedron Letters, Vol. 38, No. 36, pp. 6407-6410, 1997

0040-4039/97 $17.00 + 0.00

PII: S0040-4039(97)01482-2

Synthesis of Sulfone-Substituted Furan Chromophores with High Molecular Hyperpolarizability

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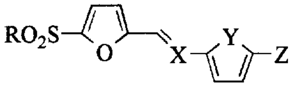
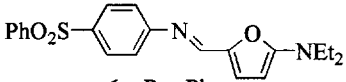
ABSTRACT: A series of sulfone-substituted furan chromophores were synthesized which showed high molecular hyperpolarizabilities as measured by solvatochromism, and good transparency in the visible region. © 1997 Elsevier Science Ltd.

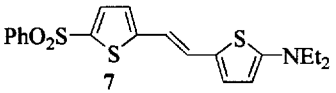
The synthesis of organic chromophores as nonlinear optical (NLO) materials has attracted much attention in late years.[1] They could be used in optical modulation, molecular switching, optical memory, and frequency doubling applications.[1b, 2] Recently, it has been revealed that the products of dipole moment and molecular hyperpolarizability ($\mu\beta$) of heterocyclic moieties are higher than those of the benzene analogs.[3] Besides the common accepting groups, the sulfone group has been shown in the benzene-based π-conjugated systems as a good acceptor substituent which is synthetically flexible and has broad transparency range in the visible spectrum.[4] We have also achieved the first synthesis of sulfone-substituted thiophene chromophores which exhibit good optical and thermal properties.[5] Here we report the synthesis, UV-VIS absorption spectrum, and second-order nonlinear optical properties of a series of sulfone-substituted furan chromophores **1-6** bearing the π-bridge of C=C or C=N. We will compare the structural effect of furan, thiophene, and benzene moiety on NLO properties. A hydroxyl group has also been attached to the amino donor group for the preparation of polymer films.



1, R = Ph, X = CH, Y = CH=CH, Z = NMe_2
2a, R = Ph, X = CH, Y = S, Z = NEt_2
2b, R = CH_3, X = CH, Y = S, Z = NEt_2
3, R = Ph, X = CH, Y = O, Z = NEt_2
4a, R = Ph, X = N, Y = CH=CH, Z = NMe_2
4b, R = CH_3, X = N, Y = CH=CH, Z = NMe_2
5a, R = Ph, X = N, Y = CH=CH, Z = $N(Et)(CH_2CH_2OH)$
5b, R = CH_3 , X = N, Y = CH=CH, Z = $N(Et)(CH_2CH_2OH)$



6a, R = Ph
6b, R = CH_3



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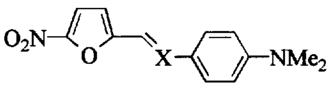
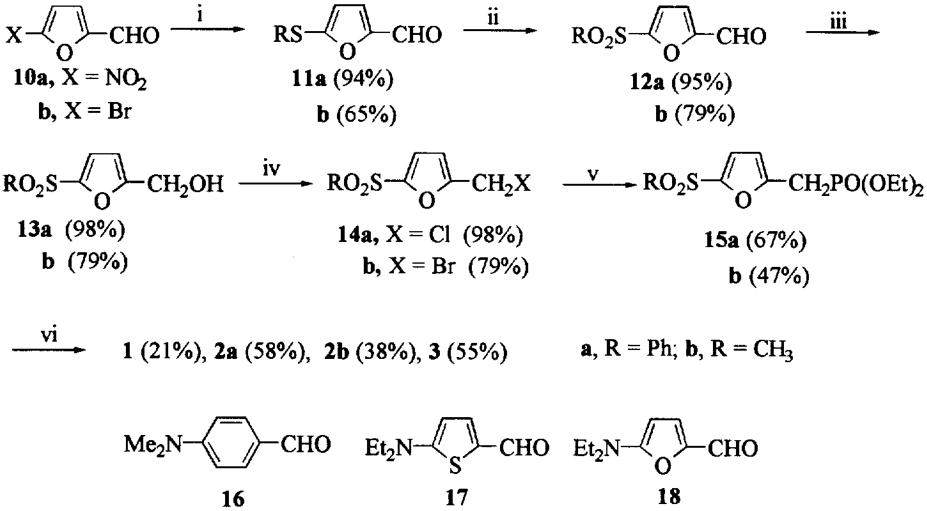


8, X = CH
9, X = N

The general methodology for the synthesis of these sulfone-substituted furan chromophores **1-3** is shown in Scheme 1. Reaction of compounds **10a** and **10b** with sodium phenylthiolate and sodium methylthiolate gave **11a**[6] and **11b**, respectively. The sulfides **11** were then oxidized by MCPBA (2.2 equiv) to the sulfones **12**.

Reduction of compounds **12** with sodium borohydride gave the alcohols **13**. Treatment of **13a** with thionyl chloride gave the chloro compound **14a**, whereas reaction of **13b** with phosphorus tribromide gave the bromo compound **14b**. Phosphonate products **15** were obtained by reactions of **14** with triethyl phosphite. Sulfone-substituted furan chromophores **1-3** were then prepared by the Wittig-Horner condensation reactions of phosphonates **15** with 4-*N*,*N*-dimethylaminobenzaldehyde (**16**), 5-*N*,*N*-diethylamino-2-thiophenecarbalde- hyde (**17**) or 5-*N*,*N*-diethylamino-2-furancarbaldehyde (**18**).

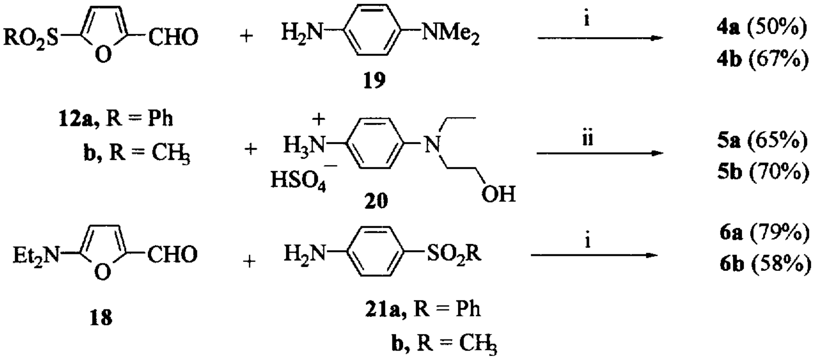
On the other hand, the furan-containing imino dyes **4-6** were more easily made (Scheme 2). Condensation of compounds **12a** and **12b** with 4-*N*,*N*-dimethylaminoaniline (**19**) and *N*-ethyl-*N*-(2-hydroxyethyl)-1,4-phenylenediamine sulfate monohydrate (**20**) gave the imino dyes **4** and **5**, respectively. Condensation of aldehyde **18** with 4-(phenylsulfonyl)aniline (**21a**) and 4-(methylsulfonyl)aniline (**21b**)[7] gave the corresponding imines **6a** and **6b** in good yields.



Scheme 1 *Reagents and conditions*: i, NaSPh or $NaSCH_3$, THF, rt, 0.5-5 h; ii, MCPBA, CH_2Cl_2, rt, 2 h; iii, $NaBH_4$, EtOH, rt, 30 min; iv, $SOCl_2$ or PBr_3, CH_2Cl_2, rt, 24 h; v, $P(OEt)_3$, 140 °C, 24 h; vi, NaH, **16**, or **17**, or **18**, THF, rt.

The UV-VIS absorptions of compounds **1-6** show that the λ_{max} values obtained in dioxane are all below 440 nm, and have virtually no absorptions at 500 nm as judged by their λ_{cutoff} values (Table 1). The phenylsulfones **2a** and **4a-6a** have slightly higher λ_{max} values and lower charge-transfer energies than the corresponding methylsulfones **2b** and **4b-6b**. It is very interesting to note that furan-containing compounds **2a** and **3** show significant blue shifts when compared with the thiophene analog **7**[5b] : 15 nm for **2a**, and 20 nm for **3** in 1,4-dioxane. Chromophores **1** and **4** containing the weak electron-withdrawing sulfone group have much shorter absorption peaks than the corresponding nitro-substituted compounds **8**[3a] and **9**[8]. The greater transparency of **1-6** should make them more suitable for developing the blue-green laser lights by the frequency-doubling technique.

The molecular hyperpolarizabilities ($\mu_g\beta$) of chromophores **1-6** were estimated by solvatochromism.[9]



Scheme 2 *Reagents and conditions*: i, H_2SO_4, EtOH, rt, 2 h; ii, Et_3N, CH_2Cl_2, rt, 2 h.

Table 1. UV-VIS absorptions, μ_{eg}, μ_g $(\mu_e - \mu_g)$, $\mu_g\beta$ values, $\mu_g\beta_0$ values for PNA, and compounds **1-9**.

Compound	λ_{max} / nm	n_{eg}[a] / cm^{-1}	λ_{cutoff} / nm	ε cm^2mole^{-1}	μ_{eg} Debye	μ_g $(\mu_e - \mu_g)$ $Debye^2$	$\mu_g\beta$[b] / 10^{-48} esu	$\mu_g\beta_0$ / 10^{-48} esu
1	385	25974	448	23252	6.0	51	243	101
2a	435	22988	507	23345	5.7	46	395	108
2b	422	23696	475	28282	6.0	38	300	93
3	430	23258	491	14928	4.7	48	257	75
4a	409	24449	480	23565	6.0	71	502	168
4b	406	24630	497	23189	6.0	51	320	115
5a	416	24038	497	30099	6.7	82	728	239
5b	412	24278	470	20528	5.7	72	439	149
6a	410	24390	501	29365	7.0	104	959	327
6b	401	24937	463	34535	7.1	47	428	151
7	450	22222	518	22182	7.8	66	1364	312
8	478[c]	20920	-	-	-	-	572[c,d]	-
9	482[e]	20746	-	-	-	-	690[e,f]	392
PNA	352	28409	-	17220	4.7	52	110	55

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[a] $n_{eg}=1/\lambda_{max}$ [b] Estimated for a fundamental wavelength of 1064 nm. [c] Ref 3a. [d] $\mu_g = 6.9$ debye, $\beta = 83 \times 10^{-30}$ esu. [e] Ref 8. [f] Measured by EFISH with a fundamental wavelength of 1579 nm.

The zero-frequency $\mu_g\beta_0$ values were corrected with a two-level model.[10] The $\mu_g\beta$ and $\mu_g\beta_0$ values for compounds **1-6** are 1.8-8.7 times and 1.0-5.9 times that of **PNA**, respectively. Comparing the $\mu_g\beta$ values of **1**, **2a**, **3** with **7**, it is clear that the thiophene ring is more effective than the benzene and furan ring, in accord with molecular orbital calculations.[11] Comparison of **4a-6a** with **4b-6b** reveals that replacement of the methylsulfone group with the phenylsulfone group markedly increases their second-order nonlinearities ($\mu_g\beta$ values: **2a/2b** =1.3, **4a/4b** = 1.6, **5a/5b** = 1.6, **6a/6b** = 2.2; $\mu_g\beta_0$ values: **2a/2b** = 1.1, **4a/4b** = 1.5, **5a/5b** = 1.6, **6a/6b** = 2.2). The $\mu_g\beta$ values of the sulfones **4** are slightly lower than that of the nitro compound **9**. It should also be pointed out that placing the donor group on the furan ring in imino dyes **6a** and **6b** gives higher $\mu_g\beta$ values than the corresponding imino derivatives **4a** and **4b** which have the acceptor group on the furan ring ($\mu_g\beta$ value: **6a/4a** =1.9, **6b/4b** =1.3). Judging from the corresponding data for **4** and **6** in Table 1, it seems that the dominating factor is the higher μ_{eg} values of **6**. Binding **5a** or **5b** to the side chain of polymers should make them suitable for NLO films.[12]

In conclusion, we have synthesized a series of phenylsulfone- and methylsulfone-substituted furan chromophores with C=C or C=N linkage. They all show λ_{max} values below 440 nm. Their second-order optical nonlinearities as estimated by solvatochromism are slightly lower than the thiophene analogs, in accord with theoretical calculations.

Acknowledgment: Financial support of this work by the National Science Council of the Republic of China is gratefully acknowledged (NSC 86-2113-M-030-002). We also thank Dr. C.-T. Chen and Mr. S. Y. Liao for their assistance in using the solvatochromic method.

References and Notes:

1. (a) Prasad, P. N.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*, Wiley: New York, **1991**; pp. 132-174. (b) Drost, K. J.; Jen, A. K-Y.; Rao, V. P. *Chemtech*. **1995**, *25*(9), 16-25 and references cited therein.
2. Prasad, P. N.; Zhang, Y.; Gao, X.; Pan, H. *Chem. Mater.* **1995**, *7*, 816-821.
3. (a) Cheng, L.T.; Tam, W.; Marder, S. R.; Stiegman, A, E.; Rikken, G.; Spangler, C. W. *J. Phys. Chem.* **1991**, *95*, 10643-10652. (b) Rao,V. P.; Jen, A. K-Y.; Wong, K. Y.; Drost, K. J. *Tetrahedron Lett.* **1996**, *37*, 1747-1750. (c) Jen, A. K-Y.; Rao,V. P.; Wong, K. Y.; Drost, K. J. *J. Chem. Soc., Chem. Commun.* **1993**, 1118-1120.
4. Ulman, A.; Willand, C. S.; Kohler, W.; Robello, D. S.; Williams, D. J.; Handley, L. *J. Am. Chem. Soc.* **1990**, *112*, 7083-7090.
5. (a) Chou, S. S. P.; Sun, D. J.; Lin, H. C.; Yang, P. K. *J. Chem. Soc., Chem. Commun.* **1996**, 1045-1046. (b) Chou, S. S. P.; Sun, D. J.; Huang, J. Y.;Yang, P. K.; Lin, H. C. *Tetrahedron Lett.* **1996**, *37*, 7279-7282.
6. (a) Kada, R.; Knoppova, V.; Kovac, J.; Balag, M. *Collect. Czech. Chem. Commun.* **1980**, *45*, 2360-2363. (b) Kada, R.; Ilavsky, D.; Stetinova, I.; Zalibera, L.; Padour, J. *Collect. Czech. Chem. Commun.* **1994**, *59*, 444-452.
7. Courtin, A. *Helv. Chim. Acta.* **1983**, *66*, 1046-1052.
8. Kuhn, H.; Robilllard, J. *Nonlinear Optical Matericals*, CRC Press Inc: Florida, USA, **1992**, 203-209.
9. (a) Paley, M. S.; Harris, J. M. *J. Org. Chem.* **1989**, *54*, 3774-3778. (b) The solvatochromic method is based on the two-level model: $\beta(2\omega) = 3\ \omega_{eg}{}^2\ \mu_{eg}{}^2\ (\mu_e - \mu_g)/2h^2\ [(\omega_{eg})^2 - (2\omega)^2][(\omega_{eg})^2 - (\omega)^2]$, where ω_{eg} is the frequency of transition from the ground to the first excited state; ω is the angular velocity; $\omega_{eg} = 2\ \pi c n_{eg}$; $\omega = 2\ \pi c n$; n_{eg} is the wave number of transition from the ground to the first excited state; c is the speed of light; h is Planck constant 6.6256×10^{-27} erg sec. When each side is timed by μ_g, a new equation is obtained: $\mu_g\ \beta\ (2\omega) = 3\ n_{eg}{}^2\ \mu_{eg}{}^2\ \mu_g(\mu_e - \mu_g)/2h^2\ c^2[(n_{eg})^2 - (2n)^2]\ [\ (n_{eg})^2 - (n)^2]$, where μ_{eg} is related to the intensity of transition and the integral area under the UV-VIS spectrum band; $\mu_g(\mu_e - \mu_g)$ can be calculated from the solvatochromic shift of the relevant absorption bands by means of the McRae equation; μ_g is dipole moment of the ground state; μ_e is dipole moment of the excited state.
10. Oudar, J. L.; Chemla, D. S. *J. Chem. Phys.* **1977**, *66*, 2664-2668.
11. Morley, J. O. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 3009-3013.
12. Chen, T. A.; Jen, A. K-Y.; Cai, Y. *J. Am. Chem. Soc.* **1995**, *117*, 7295-7296.

(*Received in Japan* 19 *May* 1997; *revised* 15 *July* 1997; *accepted* 18 *July* 1997)