

## Synthesis and Nonlinear Optical Property of a Series of New Chromophores Containing Furan Ring as the Only Conjugation Bridge

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**Abstract:** This paper reports the synthesis and the nonlinear optical property of a series of new chromophores which contain furan ring as the only conjugation bridge for the first time. They are characterized by UV-VIS, FT-IR,  $^1\text{H}$  NMR, MS and elemental analysis. Their dipole moment and the first-order molecular hyperpolarizability ( $\beta$ ) are calculated and compared with those of the analogues containing either benzene or thiophene as the conjugation bridge.

**Keywords:** 5-Diethylamino-2-furaldehyde, chromophores, nonlinear optical materials, organic synthesis, the first-order molecular hyperpolarizability ( $\beta$ ).

Organic second-order nonlinear optical (NLO) materials have attracted much attention for their potential applications involving optical modulation, molecular switching, optical memory and frequency doubling<sup>1</sup>. The appropriate second-order NLO chromophores should exhibit the following properties: large first-order molecular hyperpolarizability ( $\beta$ ), good chemical and thermal stability and wide optical transparency<sup>2</sup>.

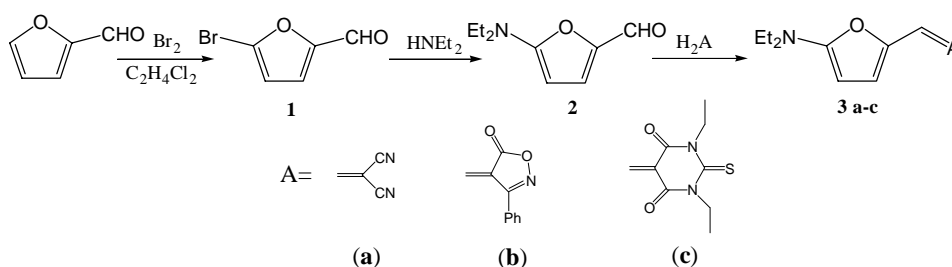
According to the theoretical results, incorporating thermally stable five-membered heterocycle into chromophores can increase the first-order molecular hyperpolarizability ( $\beta$ ) due to the highly efficient conjugation as a result of the lower resonance stabilization energy of heterocyclic compounds than that of benzene analogues<sup>3</sup>. However, although there is much research on the thiophene ring, little attention has been put on the furan ring<sup>4,7</sup>, in which furan ring is commonly used as a part of conjugation bridge. Since there is interaction between different conjugation systems, the role of furan ring in the molecule is vague. In order to investigate the influence of the furan ring as conjugation bridge on the first-order molecular hyperpolarizability ( $\beta$ ), a series of (E)-5-diethylaminofuran chromophores **3a-c** with various acceptors have been synthesized for the first time.

### Experimental

The furfural was purified by fractional distillation. 1, 2-Dichloroethane was dried over

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**Scheme 1** The synthetic route of the chromophores **3a-c**

CaCl<sub>2</sub>. The bromine was dried over P<sub>2</sub>O<sub>5</sub>. The ethanol was dried by refluxing with sodium. The malononitrile is purified by vacuum distillation. All the other reagents and solvents were used without further purification.

<sup>1</sup>H NMR spectra were obtained using a Varian Mercury 300 spectrometer. FT-IR spectra were measured with a Shimadzu FT-IR 8000 series in the region of 4000-400cm<sup>-1</sup> using KBr tablet. UV-Visible spectra were determined with a Shimadzu 160A spectrometer. FAB-MS spectra were used with VJ-ZAB-3F-Mass spectrometer.

Following the method of references<sup>8,9</sup>, compounds **1** and **2** were prepared.

#### Preparation of chromophores **3a-c**

To an ethanol solution of 5-diethylamino-2-furfuraldehyde was added an ethanol solution of an equimolar malononitrile, 5-phenylisoxazolone or 1,3-diethyl-2-thiobarbituric acid. A catalytic amount of piperidine was added and then refluxed for about 6 hours. When the reaction mixture cooled, the precipitate was collected then recrystallized from ethanol.

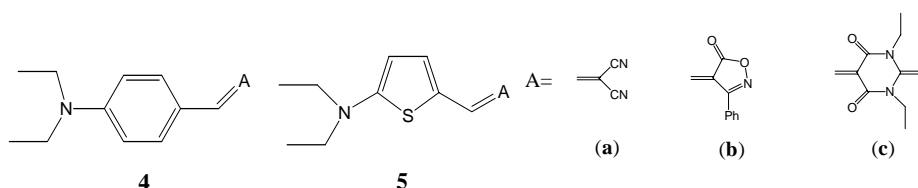
**3a**: yield: 70%; mp 129-130°C; IR (KBr): 2199, 1632 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300MHz, δ ppm), 1.29 (t, 6H, J = 6.9Hz, 2CH<sub>3</sub>), 3.51 (q, 4H, J = 6.9Hz, 2CH<sub>2</sub>), 5.50 (d, 1H, J = 4.2 Hz, CH), 6.73 (s, 1H, CH), 7.07 (d, 1H, J = 3.9Hz, CH); MS (FAB), *m/z* (%): 215 (M<sup>+</sup>, 100); anal. calcd. for C<sub>12</sub>H<sub>13</sub>N<sub>3</sub>O: C, 66.94; H, 6.10; N, 19.52. Found: C, 66.58; H, 6.40; N, 19.88. **3b**: yield: 63%; mp 182-184°C; IR (KBr): 1691, 1635 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300MHz, δ ppm), 1.31 (t, 6H, J = 6.9Hz, 2CH<sub>3</sub>), 3.52 (q, 4H, J = 6.9Hz, 2CH<sub>2</sub>), 5.84 (d, 1H, J = 3.9Hz, CH), 7.12 (s, 1H, CH), 7.53 (m, 5H, C<sub>6</sub>H<sub>5</sub>), 9.26 (d, 1H, J = 3.9Hz, CH); MS (FAB), *m/z* (%): 311 (M<sup>+</sup>+1, 100); anal. calcd. for C<sub>18</sub>H<sub>18</sub>N<sub>2</sub>O<sub>3</sub>: C, 69.65; H, 5.85; N, 9.03. Found: C, 70.07; H, 5.58; N, 8.72. **3c**: yield: 80%; mp 165-167°C; IR (KBr): 1674, 1639 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300MHz, δ ppm), 1.22-1.35 (m, 12H, 4CH<sub>3</sub>), 3.56 (q, 4H, J = 6.9Hz, 2CH<sub>2</sub>), 4.60 (q, 4H, J = 6.9Hz, 2CH<sub>2</sub>), 5.88 (d, 1H, J = 4.8Hz, CH), 8.04 (s, 1H, CH), 9.22 (d, 1H, J = 4.8Hz, CH); MS (FAB), *m/z* (%): 349 (M<sup>+</sup>, 100); anal. calcd. for C<sub>17</sub>H<sub>23</sub>N<sub>3</sub>O<sub>3</sub>S: C, 58.42; H, 6.65; N, 12.03. Found: C, 58.37; H, 7.12; N, 11.81.

### Results and Discussion

Compound **2** is the key intermediate for the synthesis of the chromophores **3**, **2** was synthesized through aromatic nucleophilic substitution of compound **1**. Some water is added to activate the bromine atom in 5-bromo-2-furaldehyde. In this paper, a new convenient purification procedure, vacuum distillation of the extract, has been explored. There is no low boiling-point fraction during distillation and the purity is good enough as evidenced by <sup>1</sup>H NMR. As far as we know, it is the first time to use the vacuum distillation for purification of the 5-diethylamino-2-furaldehyde.

The properties of chromophores **3a-c** are shown in **Table 1**. The first-order molecular hyperpolarizability ( $\beta$ ) of **3a-c** were calculated by using MOPAC in Chem 3D Pro<sup>7</sup>. For the purpose of comparison, the  $\beta$  values of benzene analogues **4a-c** and thiophene analogues **5a-c** ( their structures are shown in **Scheme 2** ) were also calculated. The ground state dipole moment ( $\mu$ ) of all the compounds are also listed.

**Scheme 2** The structure of **4a-c** and **5a-c**



**Table 1** The properties of **3a-c** and the benzene and thiophene analogues

Compounds	$\lambda_{\max}$ ( nm )		$\mu^*$ ( $10^{-18}$ esu )	$\beta_0^*$ ( $10^{-30}$ esu )
	CHCl <sub>3</sub>	Dioxane		
<b>3a</b>	467.5	461.0	7.655	30.9
<b>3b</b>	510.0	507.5	8.793	36.5
<b>3c</b>	511.0	508.0	8.125	38.7
<b>4a</b> <sup>10</sup>	-	419	6.116	20.4
<b>4b</b>	-	-	7.233	27.7
<b>4c</b> <sup>3</sup>	500	-	5.737	26.8
<b>5a</b> <sup>11</sup>	-	-	8.506	32.0
<b>5b</b>	-	-	9.046	35.7
<b>5c</b> <sup>11</sup>	-	-	8.174	35.9

\*All of the  $\mu$ ,  $\beta_0$  values were calculated by MOPAC in chem 3D Pro.

It can be seen in **Table 1** that all  $\beta$  and  $\mu$  values of **3a-c** are larger than those of the corresponding benzene analogues **4a-c**, and similar to those of the corresponding thiophene analogues **5a-c**. These computational results demonstrate that the intramolecular charge transfer efficiency in furan ring is almost the same as that in the thiophene ring, while higher than that in benzene ring.

**Table 1** also lists  $\lambda_{\max}$  of **3a-c**, **4a** in dioxane and **3a-c**, **4c** in chloroform. By comparison of  $\lambda_{\max}$  of **3a** and **4a** in dioxane, or **3c** and **4c** in chloroform, red-shift phenomena can be observed, 42 nm for **4a** over **3a** in dioxane and 11 nm for **4c** over **3c** in chloroform respectively. Experimental measurement of the first-order molecular hyperpolarizability ( $\beta$ ) value is currently in progress.

In conclusion, we have synthesized a series of new nonlinear optical chromophores containing furan ring as the conjugation bridge. These compounds have given some information that the furan ring as conjugation bridge has influenced the first-order molecular hyperpolarizability ( $\beta$ ).

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### References

1. S. R. Marder, B. Kippelen, A. K-Y. Jen, N. Peyghambarian, *Nature*, **1997**, *388*, 845.
2. C. R. Moylan, R. J. Twieg, V. Y. Lee, S. A. Swanson, K. M. Betterton, R. D. Miller, *J. Am. Chem. Soc.*, **1993**, *115*, 12599.
3. L. T. Cheng, W. Tam, S. H. Stevenson, S. R. Marder, A. E. Stiegman, G. Rikken, C. W. Spangler, *J. Phys. Chem.*, **1991**, *95*, 10643.
4. S. Song, S. J. Lee, B. R. Cho, D. H. Shin, K. H. Park, C. J. Lee, N. Kim, *Chem. Mater.*, **1999**, *11*, 1406.
5. B. R. Cho, K. N. Son, S. J. Lee, T. I. Kang, M. S. Hon, *Tetrahedron Lett.*, **1998**, *39*, 3167.
6. S. S. P. Chom, C. H. Shen, *Tetrahedron Lett.*, **1997**, *38*, 6407.
7. J. Hua, W. Zhang, J. Luo, J. Qin, Y. Shen, Y. Zhang, Z. Lu, *J. Chem. Research ( S )*, **2001**, *11*, 418.
8. C.A. 49, 10261 ( **1955** ).
9. C.A. 72, 31523 ( **1970** ).
10. V. P. Rao, A. KY. Jen, J. B. Caldwell, *Tetrahedron Lett.*, **1994**, *35*, 3849.
11. L. T. Cheng, W. Tam, U. S. Patent: 5,272,218 ( Dec. 21 ), **1993**.

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