Synthesis, Crystal Structure, and Nonlinear Optical Property of Two New Chromophores Containing Furan Ring as a Conjugation Bridge

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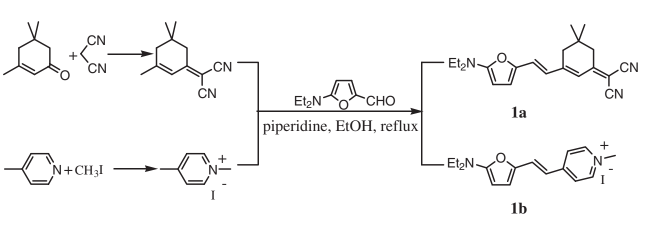
(Received October 15, 2002; CL-020880)

Two new organic chromophores containing furan ring as a conjugation bridge located near the donor have been synthesized and characterized by X-ray single crystal structure determination. Their first molecular hyperpolarizability (β) are measured by Hyper-Rayleigh Scattering (HRS) technique.

Organic second-order nonlinear optical (NLO) chromophores have attracted considerable research interests during the past decade due to their potential applications in optical communications, molecular switching, optical memory and frequency doubling.[1] The appropriate second-order NLO chromophores should exhibit the following properties: large first molecular hyperpolarizability (β), good chemical and thermal stability and wide optical transparency.[2]

According to the bond length alternation (BLA) theory,[3] incorporating thermally stable five-membered heteroaromatics into chromophores can increase the first-order molecular hyperpolarizability due to the highly efficient conjugation as a result of the lower resonance stabilization energy of heterocyclic compounds than that of benzene analogues.[4] However, although there is much research on the thiophene ring, of which resonance stabilization energy is higher than that of furan ring, little attention has been put on the furan ring.[4,5] In order to investigate the influence of the furan ring as a conjugation bridge on the values of β, two (*E*)-5-diethylaminofuran chromophores with different acceptors (**1a** and **1b**) have been synthesized for the first time. Their synthetic routes are shown in Scheme 1. In these two chromophores the electron-rich furan ring is located near the donor, and may play a role of an auxiliary donor.[6]



Scheme 1.

Characterization of the chromophores was carried out by ^{1}H-NMR, IR, MS, and elemental analyses,[7] and supported by the X-ray structure determination of chromophore **1a**.[8] The ORTEP drawing of **1a** is shown in Figure 1. From the bond length data, the value of BLA of chromophore **1a** (BLA is defined as the average difference in length between adjacent single and double bonds[9]) could also be computed out as 0.0046 nm. This value is close to 0.004 nm, the optimal value according to the BLA theory when chromophores reach to their maximal β values.

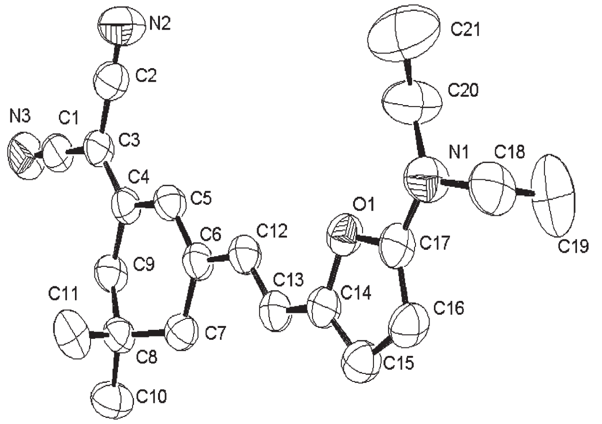


Figure 1. The ORTEP drawing of **1a** with thermal ellipsoids drawn at the 50% probability level. All hydrogen atoms are omitted for clarity. Representative bond lengths (Å) are as follows: C17-C16 = 1.362(3), C16-C15 = 1.387(3), C15-C14 = 1.359(3), C14-C13 = 1.395(3), C13-C12 = 1.353(3), C12-C6 = 1.425(3), C6-C5 = 1.363(2), C5-C4 = 1.507(2), C4-C3 = 1.375(2).

The first molecular hyperpolarizability of the chromophores **1a** and **1b** was measured by Hyper-Rayleigh Scattering (HRS) technique[10] in chloroform using the fundamental excitation wavelength of 1064 nm. The known β value for *p*-nitroaniline (*p*-NA) in chloroform (23×10^{-30} esu)[11] was used as an external reference. The measured β values of chromophores **1a** and **1b** were found to be 593×10^{-30} and 1196×10^{-30} esu, respectively, and the static β_0 values obtained from the two-level approximation model were extrapolated to be 136×10^{-30} esu and 131×10^{-30} esu, respectively. Their absorption maxima (λ_{max}) in chloroform are at 617 and 571 nm respectively.

In summary, we have synthesized two new chromophores containing furan ring as a conjugation bridge located near the donor. They all show relatively large β values.

The work was supported by a grant from the National Key Fundamental Research Program of China and by National Science Foundation of China.

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7 The yield, melting point, IR (KBr, cm^{-1}), NMR (300 MHz), MS, and elemental analysis data for these compounds are as follows: **1a**: yield 72%; mp 148-150 °C; IR (KBr): 2211 (C≡N), 1617 (C=C); ^{1}H-NMR ($CDCl_3$): δ 1.03-1.32 (m, 12H), 2.35 (s, 2H), 2.52 (s, 2H), 3.41 (q, 4H), 3.71 (d, 1H, CH), 5.17 (d, 1H, $J = 3.9$ Hz, CH), 6.44 (d, 1H, $J = 15.0$ Hz, CH), 6.62-6.69 (m, 2H); MS (FAB), m/z: 335 (M^+, 100%); Anal. Calcd for $C_{21}H_{25}N_3O$: C, 75.22; H, 7.46; N, 12.53. Found: C, 75.64; H, 7.25; N, 12.76. **1b**: yield 78%; mp 193-195 °C; IR (KBr): 1649 (C=N), 1614 (C=C); ^{1}H-NMR($CDCl_3$): δ 1.27 (t, 6H), 3.46 (q, 4H), 4.23 (s, 3H), 5.34 (d, 1H, $J = 3.9$ Hz, CH), 6.28 (d, 1H, $J = 15.6$ Hz, CH), 6.98 (d, 1H, $J = 3.9$ Hz, CH), 7.20 (d, 1H, $J = 15.6$ Hz, CH), 7.48 (d, 2H, $J = 6.9$ Hz, CH_2), 8.39 (d, 2H, $J = 6.9$ Hz, CH_2); MS (FAB), m/z: 257 (M^+-127, 100%); Anal. Calcd for $C_{16}H_{21}N_2OI$: C, 50.00; H, 5.47; N, 7.29. Found: C, 49.79; H, 5.53; N, 7.65.

8 Crystal data for **1a**: $C_{21}H_{25}N_3O$; $M_r = 335.44$, monoclinic, $a = 9.5863(3)$ Å, $b = 15.2532(4)$ Å, $c = 13.6325(4)$ Å, $\alpha = 90$, $\beta = 98.213(10)$, $\gamma = 90$, $V = 1972.92(10)$ Å^3, $D_{calc} = 1.129$ g/cm^3, $T = 293(2)$ K, space group, $P2_1/n$, $Z = 4$, F(000) = 720, μ(Mo Kα) = 0.071 mm^{-1}, 8762 reflections measured, 4527 unique ($R_{\text{int}} = 0.0393$), 1847 observed ($> 2\sigma$), final residuals $R_1 = 0.0472$, $\omega R_2 = 0.1045$ $[I > 2\sigma(I)]$; $R_1 = 0.1309$, $\omega R_2 = 0.1337$ (all data).

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