Synthesis and Nonlinear Optical Properties of *p*-(Dimethylamino)benzylidene Dyes Containing Different Acceptors

Qingdong Zheng, Zuguang Yao,* Jiqi Cheng,† Yaochun Shen,† and Zuhong Lu†
Institute of Fine Chemicals, East China University of Science and Technology, Shanghai 200237, P.R.China
† *National Laboratory of Molecular and Biomolecular Electronics, Southeast University, Nanjing 210096, P.R.China*

(Received September 27, 2000; CL-000888)

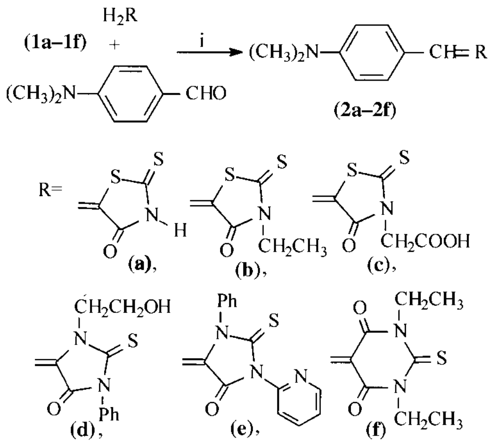
Several *p*-(dimethylamino)benzylidene dyes were synthesized and their evaluation of β using Hyper-Rayleigh Scattering (HRS) technique was reported. The results show that these dyes have enhanced second-order hyperpolarizabilities.

Recent years have witnessed a dramatic growth of multidisciplinary research activity involving materials that exhibit nonlinear optical (NLO) behavior.[1,2] Donor–acceptor substituted conjugated compounds are well known for their linear electro optic (EO) applications. Most of the EO materials which possess an electro optic coefficient greater than that of $LiNbO_3$ (30 pm/V at 1.3 μm) have an absorption maximum greater than 600 nm. Such absorption can result in high optical losses at diode wavelengths. Consequently, finding improved transparency/nonlinearity tradeoff compounds is of great interest.

Recently, thiobarbituric acid has been often used as a strong acceptor in the donor–acceptor substituted conjugated compounds for nonlinear optics.[3,4] However, little experimental work has been reported for the compounds which use rhodanine or thiohydantoin as an acceptor. Because most of the data report βμ values (the scalar product of the vectorial component of the second-order hyperpolarizability tensor and the dipole moment) rather than β, it is difficult to compare their hyperpolarizabilities. Our objective in this study is to design and synthesize several push-pull compounds containing different acceptors, and to study their properties using HRS method and compare their nonlinear optical properties.

Donor–acceptor compounds studied in this work are shown in Scheme 1. Compounds (**2a**, **2b**, **2f**) have been reported in the literature.[5–7] *p*-(Dimethylamino)benzaldehyde used in this study is commercially available. Rhodanine, thiohydantoin and thio-barbituric acid were synthesized according to the reference.[8–11] Knoevenagel condensation of compounds (**1a**–**1c**, **1f**) with *p*-(dimethylamino)benzaldehyde in the presence of Et_3N/EtOH yielded compounds (**2a**–**2c**, **2f**). However, this condition proved ineffective in the case of compound (**2d**, **2e**). It led to both poor yields and purification problems. Compounds (**2d**, **2e**) were synthesized by Knoevenagel condensation of compounds (**1d**, **1e**) with *p*-(dimethylamino)benzaldehyde in the presence of Ac_2O, NaOAc/HAc. Yields and melting points of all the compounds are shown in the notes.[12] They are identified by ^1H NMR, IR and elemental analysis.[12]

Second-order hyperpolarizabilities of all the compounds were determined using Hyper-Rayleigh Scattering (HRS) technique described elsewhere.[13,14] External reference method (ERM) was used to extract the β values of the compounds and *p*-nirtoaniline (*p*-NA) was used as a reference solution whose β value is known. The HRS data obtained in methanol solvent for the compounds are presented in Table 1.



Reagents and conditions: (a)–(c), (f) : Et_3N/EtOH,
(d), (e) : Ac_2O, NaOAc/HAc

Scheme 1.

Table 1. Optical properties of *p*-(dimethylamino)benzylidene dyes

Compounds	λ max(nm) in methanol	β (10^{-30}esu) at λ =1060nm	β_0(10^{-30}esu)
2a	450	2200	514
2b	463	2488	477
2c	460	2070	424
2d	447	550	133
2e	454	930	206
2f	495	1100	116

All of the acceptors used in this work have strong electron-accepting ability which due to the gain of partial aromaticity of these acceptors in the resonance charge-separated state. Results in Table 1 show that the compounds with rhodanine methine acceptor have 3 times larger second-order hyperpolarizabilities than that with thiobarbituric acid, and the compounds with thiohydantoin methine acceptor have comparable hyperpolarizabilities than that with thiobarbituric acid. Compounds (**2a**–**2c**) differ in substitute groups and comparison of their β_0 values shows that substitute groups of the acceptor moiety have minor influence on the second-order nonlinearity. Their electronic absorption spectrum in methanol shows that the λ_{max} of the compounds **2a**–**2e** are shorter than **2f**. Comparison of the β values of compounds **2a**–**2f** reveals that rhodanine methine acceptor and thiohydantoin methine acceptor are strong electron-acceptors and produce significantly enhanced molecular optical nonlinearity.

In conclusion, we have synthesized a series of compounds containing different acceptors with enhanced molecular optical nonlinearity. These molecules are likely the candidates to be used as the pendent side chains in polymer flims and further work is in the progress.

Reference and Notes

1 S. R. Marder, B. Kippelen, A.K.-Y. Jen, M. Reyghambarian, *Nature,* **388**, 845 (1997).

2 T. Verbiest, S. Houbrechts, M. Kauranen, K. Clays, and A. Persoons, *J. Mater. Chem.*, **7**, 2175 (1997).

3 S. R. Marder, L. T. Cheng, B. G. Tiemann, A. C. Friedli, M. Blanchare-Desce, J. W. Perry, and J. Skindhoj, *Science*, **263,** 511 (1994).

4 L. R. Dalton, A. W. Harper, R. Ghosn, W. H. Steier, M. Ziari, H. Fetterman, Y. Shi, R. V. Mustacith, A. K.-Y. Jen, and K. J. Shea, *Chem. Mater.*, **7**, 1060 (1995).

5 S.M. Ramsh, G.S. Antonova, A. I. Ginak, and E. G. Sochilin, *Zh. Org. Khim.*, **11**, 1755 (1975); *Chem. Abstr.*, **83**, 193156a (1975).

6 S. R. Marder, L. T. Cheng, B. G. Tiemann, A. C. Friedli, M. Blanchard-Desce, J. W. Perry, and J. Skindhøj, *Science*, **263**, 511 (1994).

7 G. A. Chamberlain and R. E. Malpas, *Faraday Dicuss. Chem. Soc.*, **70**, 299 (1981).

8 F. C. Brown, C. K. Bradsher, E. C. Morgan, M. Tetenbaum, and P. Wilder, *J. Am. Chem. Soc.*, **78**, 384 (1956).

9 K. Sakazume, S. Itoh, and S. Sato, U. S. Patent 3625698 (1971); *Chem. Abstr*., **73**, 40470s (1969).

10 B. Edward and H. Knott, U. S. Patent 2839403 (1958); *Chem. Abstr*., **53**, 944e (1959).

11 L. G. S. Brooker, G. H. Keyes, R. H. Sprague, R. H. Vandyke, E. Vanlare, G. Vanzandt, and F. L.White, *J. Am. Chem. Soc.*, **73**, 5326 (1951).

12 The yield(%), mp(°C), IR(KBr, ν(C=O;C=S),cm^{-1}), ^{1}H NMR(500 MHz), and elemental analysis data for these compounds are as follows. **2a**: yield 58.0; mp 250–251; IR 1685 1195; ^{1}H NMR($CDCl_3$) δ 3.04 (s, 6H, $N(CH_3)_2$), 6.84, 7.44 (2d, 4H, *J* = 9.0Hz, C_6H_4), 7.54 (s, 1H, =CH–), 13.75 (bs, 1H, NH); Anal. Calcd for $C_{12}H_{12}N_2OS_2$: C, 54.52; H, 4.54; N, 10.60%. Found: C, 54.29; H 4.47; N, 10.69%. **2b**: yield 54.0; mp 222–223; IR 1720 1700 1195; ^{1}H NMR($CDCl_3$) δ 3.07 (s, 6H, $N(CH_3)_2$), 4.73 (s, 2H, $–CH_2COOH$), 6.86, 7.52 (2d, 4H, *J* = 9.0 Hz, C_6H_4), 7.66 (s, 1H, =CH–), 13.40 (bs, 1H, OH); Anal. Calcd for $C_{14}H_{16}N_2OS_2$: C, 57.50; H, 5.52; N, 9.58%. Found: C, 57.37; H, 5.30; N, 9.59%. **2c**: yield 60.0; mp 159–161; IR 1695 1195; ^{1}H NMR(DMSO-d_6) δ 1.31 (t, 3H, *J* = 7.2 Hz, $–CH_2CH_3$), 3.12 (s, 6H, $N(CH_3)_2$), 4.21 (q, 2H, *J* = 7.2 Hz, $–CH_2CH_3$), 6.82, 7.42 (2d, 4H, *J* = 8.9 Hz, C_6H_4), 7.68 (s, 1H, =CH–); Anal. Calcd for $C_{14}H_{14}N_2O_3S_2$: C, 52.16; H, 4.38; N, 8.69%. Found: C, 51.80; H, 4.26; N, 8.66%. **2d**: yield 82.0; mp 240–241; IR 1710 1200; ^{1}H NMR(DMSO-d_6) δ 3.01 (s, 6H, $N(CH_3)_2$), 3.74 (t, 2H, *J* = 6.0 Hz, NCH_2), 4.32 (t, 2H, *J* = 6.0 Hz, CH_2OH), 4.98 (bs, 1H, OH), 6.74, 8.16 (2d, 4H, *J* = 9.1 Hz, C_6H_4), 7.06(s, 1H, =CH–), 7.37-7.54 (m, 5H, C_6H_5); Anal. Calcd for $C_{20}H_{22}N_3O_2S$: C, 65.37; H, 5.76; N, 11.43%. Found: C, 64.95; H, 5.60; N, 11.42%. **2e**: yield 80.0; mp 255–256; IR 1735 1200; ^{1}H NMR(DMSO-d_6) δ 3.13 (s, 6H, $N(CH_3)_2$), 6.19 (s, 1H, =CH–) 7.62, 7.98 (2d, 4H, *J* = 9.1Hz, C_6H_4), 7.43–8.72 (m, 9H, C_6H_5 and H of pyridine); Anal. Calcd for $C_{23}H_{20}N_4OS$: C, 68.98; H, 5.03; N, 13.99%. Found: C, 68.94; H, 4.86 N, 14.01%. **2f**: yield 86.0; mp 218–219; IR 1680 1660 1195; ^{1}H NMR($CDCl_3$) δ 1.32, 1.33 (overlap t, 6H, *J* = 7.02, 7.05 Hz, $2NCH_2CH_3$), 3.18 (s, 6H, $N(CH_3)_2$), 4.58, 4.60 (overlap q, 4H, *J* = 7.07, 7.06 Hz, $2NCH_2CH_3$), 6.73, 8.43 (2d, 4H, *J* = 9.2 Hz, C_6H_4), 8.44 (s, 1H, =CH–); Anal. Calcd for $C_{17}H_{21}N_3O_2S$: C, 61.61; H, 6.39; N, 12.68%. Found: C, 61.68; H, 6.38; N, 12.81%.

13 K. Clays and A. Persoons, *Rev. Sci. Instrum*., **63**, 3285 (1992).

14 Y. Shen, Z. Tang, M. Gui, J. Cheng, X. Wang, and Z. Lu, *Chem. Lett*., **2000**, 1140.