N-Cyano-*N'*-diethylaminophenyl-1,4-naphthoquinonediimines: New Chromophores for Second-order Nonlinear Optical Materials

Yuji Kubo,* Toyohisa Takaba, and Shinji Aramaki*†
Department of Applied Chemistry, Faculty of Engineering, Saitama University, 255 Shimo-ohkubo, Urawa, Saitama 338
†Mitsubishi Chemical Corporation, Yokohama Research Center, Kamoshida-cho, Aoba-ku, Yokohama 227

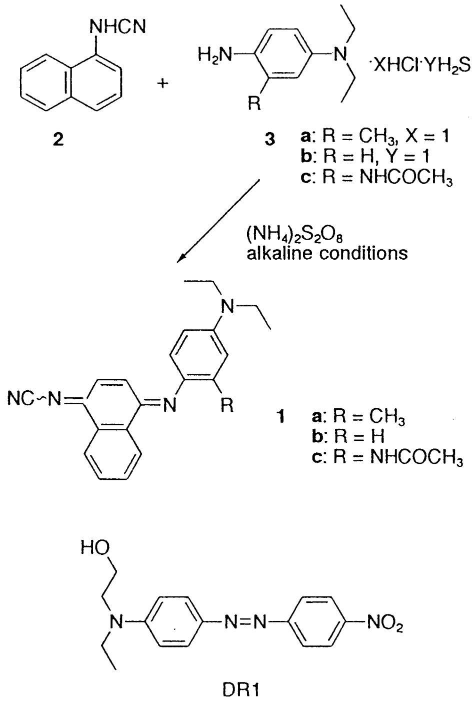
(Received November 5, 1996)

New chromophores for second-order nonlinear optical materials, *N*-cyano-*N'*-diethylaminophenyl-1,4-naphthoquinone-diimines, were proposed. The electro-optic poled polymers showed large second-order nonlinear hyperpolarizability ($\mu\beta$) in a constant electric field at incident irradiation wavelength of 1.3 μm, being 4 - 6 times than that of commonly used Disperse Red 1.

The rational design and synthesis of new chromophores possessing large values of the first molecular hyperpolarizability (β) have been recently motivated by the quest for better electro-optic (EO) materials,[1] which are essential of modern communications systems. In line with general consideration that the molecular nonlinear susceptibility may be depend on the strength of donor and acceptor groups and the π-bridge conjugation length, several kinds of second-order nonlinear optical (NLO) chromophores have been synthesized.[2] The successful exploration of such chromophores might be, however, encountered some difficulties: 1) in the case of thin-film for EO applications, an intermolecular interaction such as an aggregation takes place to result in a disturbance of polar orientation of the chromophore; 2) a longer π-conjugated system reduces nonlinearlity per the molecular mass. Thus poling studies of the chromophores are strongly desired for evaluation the nonlinearity.[2a,2d,3] Our strategy to obtain high-β performance poled polymer, in the applications of telecommunication using modulators at 1.3 or 1.55 μm, makes use of a chromophore possessing the following characteristics: 1) it has an intense charge-transfer band in visible and near-IR region to get an efficient enhancement of nonlinearlity at 1.3 or 1.55 μm, but rarely absorb light beyond 1.3 μm; 2) the molecular mass is a relatively small; 3) a steric hindrance exists in the molecule to avoid an intermolecular interaction. Previously, we proposed naphthoquinone methide-type near-IR chromophores as potential EO materials.[2d] In spite of the occurrence of the efficient NLO properties, some of the derivatives showed the propagation losses in planar waveguides at 1.3 μm.[4] Thus the improvement of the chromophore was required. In this context, a series of *N*-cyano-*N'*-diethylaminophenyl-1,4-naphthoquinonediimines **1**, the λ_{max} values of which are *ca.* 700 nm in chloroform, is another candidate. Particularly, the development of a new NLO-active chromophore possessing cyano-derived quinone-diimine type acceptor is motivated by the fact that the related bis(cyanoimide) quinoid acceptor has excellent properties with respect to potentially conductive charge-transfer complexes.[5] To date, chromophores with such an acceptor have not investigated for NLO materials.

Here, we report the synthesis of new NLO-active chromophores **1**, the $\mu\beta$ values of which have been obtained from Pockels coefficients after poling in polymer matrices in an attempt to develop new materials with useful NLO properties.

Compounds **1** were synthesized using the method as described previously[6] (Scheme 1). Starting material,1-naphthylcyanamide, **2**[7] could be quantitatively prepared by desulfurization of 1-(1-naphthyl)-2-thiourea in the presence of $Pb(OAc)_2$. The condensation reaction of **2** with aniline derivatives **3** in the presence of $(NH_4)_2S_2O_8$ under alkaline conditions produced **1**[8] in 61 - 97% yield. Poled polymers containing these chromophores were successfully prepared by the procedure as follows. Poly(methyl methacrylate) (PMMA) films (2 - 3 μm) doped with **1** were prepared by the spin-coating procedure onto an indium tin oxide (ITO) glass substrate from a cyclopentanone solution of **1**. After removing residual solvent, a thin layer of gold was deposited under vacuum onto films as a top electrode for poling. The samples were poled at 120 °C in a 0.5 $MVcm^{-1}$ electric field for 10 min. After cooling, the electric-field induced birefringence was measured using the irradiation (1.3 μm), during of which a 10 V_{rms} AC voltage was overlapped to prevent a decay of the dye orientation induced by the removal of the DC poling field. Figure 1 shows concentration dependence of obtained EO effect, Pockels coefficients,[9] for **1a** after the poling; a good linear relationship was obtained, indicating the chromophore in the poled polymer did not aggregate. Thus, the $\mu\beta$ values of **1a** could be determined from their Pockels coefficients r_{33} using an Oriented Gas Model showing in eqn. (1)



Scheme 1.

$$r_{33} = \frac{2\chi^{(2)}}{n^4}, \qquad \chi^{(2)} = \frac{Nf_\omega{}^2 f_0 f_0'(\mu\beta E_p)}{5kT_p} \qquad (1)$$

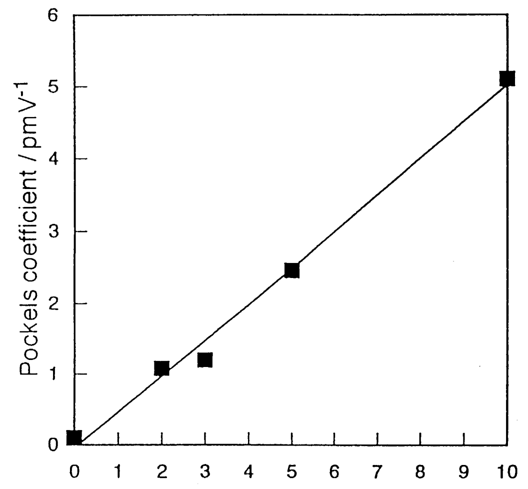


Figure 1. Concentration dependence of Pockels coefficients for **1a** after poling in 0.5 MVcm^{-1} electic field in PMMA.

where n is refractive index, N is concentration of the chromophore, f_ω and f_0 are local field factors of frequency ω (light) and 0, respectively, f_0' is the local field factor of zero frequency at the poling temperature, E_p is poling electric field, k is Boltzman's constant, and T_p is the temperature at which the molecular orientation is determined. The $\mu\beta$ value can be estimated directly from the slope of the straight line, whose value is more direct than the electric-field-induced second harmonic generation (EFISH) method.[10] The local field factor for poling electric field (E_p = 0.5 MVcm^{-1}) can be calculated from the static dielectric factor at T_p, the total value of which ($f_\omega{}^2 f_0 f_0'$) is assumed to be 7, being slightly larger than that of PMMA. T_p is also assumed to be 100 °C. These assumptions do not affect the calculation of $\mu\beta$ greatly. In order to estimate the accuracy for the measurement, we obtained the $\mu\beta$ value of well-known Disperse Red 1 (DR1) ($\mu\beta = 825 \times 10^{-48}$ esu measured at 1.3 μm), which is consistent with that ($\mu\beta = 1080 \times 10^{-48}$ esu) derived from the EFISH method. In this way, the $\mu\beta$ values of **1a** could be estimated to be 4600×10^{-48} esu. The properties for other derivatives have been evaluated in a similar way. As summarized in Table 1, Compounds **1** (the λ_{max} values of which in PMMA films are 699 - 727 nm) have $\mu\beta$ values of $(2900 - 4600) \times 10^{-48}$ esu, being 4 - 6 times that of DR1, while increments of the molecular masses are small. Taken together, these results suggested that **1** could be feasible as a NLO-active chromophore.

Table 1. Absorption maxima and $\mu\beta$ ($\omega = \omega + 0$) products in PMMA films at 1.3 μm

Compound	$\lambda_{max}{}^a$ / nm	$\lambda_{max}{}^b$ / nm	$\mu\beta$ (10^{-48} esu)^c
1a	725	719	4600 (2500)
1b	705	699	3200 (1800)
1c	736	727	2900 (1600)
DR1	-	470	825 (650)

^{a}In chloroform. ^{b}In PMMA film. ^{c}Values in parentheses represent $\mu\beta_0$, zero-frequency hyperpolarizability products obtained from the extrapolation of the measurement $\mu\beta$ values using the two-level model.[11]

The synthesis for wide range of derivatives with cyano-derived quinonediimine type acceptor, as well as the elucidation of the thermal stability and propagation loss is the subject of our current attention. Also the covalent incorporation of this chromophore into a polymer should be useful for obtaining high concentration of the chromophores and for increasing the thermal stability of the poled polymers.

This work was partially supported by a Grant-in-Aid for Scientific Research on Priority Areas "Light Wave Manipulation Using Organic Nonlinear Optical Materials" (No. 08236207).

References and Notes

1 "Nonlinear Optical Properties of Organic and Crystals, Vols. 1, 2," ed by D. S. Chemla and J. Zyss, Academic Press, New York (1987); "Nonlinear Optical Properties of Organic and Polymeric Materials," ed by D. J. Williams, ACS Symp. Ser., 233 (1983); "Materials for Nonlinear Optics: Chemical Perspective," ed by S. R. Marder, J. E. Sohn, and G. D. Stucky, ACS Symp. Ser., 455 (1991); S. R. Marder and J. W. Perry, *Science*, **263**, 1706 (1994).

2 a) S. R. Marder, L.-T. Cheng, B. G. Tiemann, A. C. Friedli, M. Blanchard-Desce, J. W. Perry, and J. Skindhoj, *Science*, **263**, 511 (1994); b) V. P. Rao, Y. M. Cai, and A. K-Y. Jen, *J. Chem. Soc., Chem. Commun.*, **1994**, 1689 and references cited therein; c) S. H. Kang, Y-M. Jeon, K. Kim, S. Houbrechts, E. Hendrickx, and A. Persoons, *J. Chem. Soc., Chem. Commun.*, **1995**, 635; d) Y. Kubo, S. Aramaki, Y. Okamoto, and T. Murayama, *J. Chem. Soc., Chem. Commun.*, **1995**, 969; e) C. Dhenaut, I. Ledoux, I. D. W. Samuel, J. Zyss, M. Bourgault, and H. L. Bozec, *Nature*, **374**, 339 (1995); f) M. Ahlheim, M. Barzoukas, P. V. Bedworth, M. Blanchard-Desce, A. Fort, Z.-Y. Hu, S. R. Marder, J. W. Perry, C. Runser, M. Staehelin, and B. Zysset, *Science*, **271**, 335 (1996); g) P. Boldt, G. Bourhill, C. Bräuchle, Y. Jim, R. Kammler, C. Müller, J. Rase, and J. Wichern, *J. Chem. Soc., Chem. Commun.*, **1996**, 793; h) S. M. LeCours, H-W. Guan, S. G. DiMangno, C. H. Wang, and M. J. Therien, *J. Am. Chem. Soc.*, **118**, 1497 (1996); i) S. Priyadarshy, M. J. Therien, and D. N. Beratan, *J. Am. Chem. Soc.*, **118**, 1504 (1996); j) F. Pan, M. S. Wong, V. Gramlich, C. Bosshard, and P. Günter, *J. Am. Chem. Soc.*, **118**, 6315 (1996); k) P. V. Bedworth, Y. Cai, A. Jen, and S. R. Marder, *J. Org. Chem.*, **61**, 2242 (1996); l) C.-F. Shu, W.-J. Tsai, and A. K.-Y. Jen, *Tetrahedron Lett.*, **37**, 7055 (1996); m) S.-S. P. Chou, D.-J. Sun, J.-Y. Huang, P.-K. Yang, and H.-C. Lin, *Tetrahedron Lett.*, **37**, 7279 (1996); n) X. R. Bu, H. Li, D. V. Derveer, and E. A. Mintz, *Tetrahedron Lett.*, **37**, 7331 (1996); o) H.-J. Deussen, E. Hendrickx, C. Boutton, D. Krog, K. Clays, K. Bechgaard, A. Persoons, and T. Bjornholm; *J. Am. Chem. Soc.*, **118**, 6841 (1996); C.-F. Shu, W. J. Tsai, J.-Y. Chen, A. K.-Y. Jen, Y. Zhang, and T.-A Chen, *Chem. Commun.*, **1996**, 2279.

3 D. M. Burland, R. D. Millar, and C. A. Walsh, *Chem. Rev.*, **94**, 31 (1994).

4 S. Aramaki, Y. Okamoto, T. Murayama, and Y. Kubo, *Pros. SPIE*, **2285**, 58 (1994).

5 A. Aumüller and Hüning, *Angew. Chem., Int. Ed. Engl.*, **23**, 447 (1984).

6 Y. Kubo, M. Kuwana, K. Okamoto, and K. Yoshida, *J. Chem. Soc., Perkin Trans. 1*, **1990**, 1975.

7 F. Kurzer, *Org. Synth.*, 1963, Coll. vol. 4, p. 174.

8 Data for **1a**: mp 138 - 139 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25 (t, J = 7.1 Hz, 6H), 2.45 (s, 3H), 3.46 (q, J = 7.1 Hz, 4H), 6.56 (dd, J = 2.8, 8.8 Hz, 1H), 6.70 (d, J = 3.0 Hz, 1H), 6.71 (d, J = 8.7 Hz, 1H), 7.39 (d, J = 10.1 Hz, 1H), 7.43 (d, J = 10.0 Hz, 1H), 7.60 (t, J = 7.3 Hz, 1H), 7.74 (t, J = 7.1 Hz, 1H), 8.38 (d, J = 7.8 Hz, 1H), 8.60 (d, J = 7.8 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.8, 19.2, 44.7, 109.4, 115.9, 113.8, 123.9, 125.0, 125.2, 129.1, 129.7, 130.0, 133.0, 135.4, 138.6, 138.7, 148.6, 148.7, 175.1; MS: m/z 342 (M^+), 327 (M^+ - 15); IR (KBr): 2168 cm^{-1}; Found: C. 77.2; H, 6.5; N, 16.3%. Calcd for $C_{22}H_{22}N_4$: C, 77.2; H, 6.5; N, 16.4%.

9 C. C. Teng and H. T. Man, *Appl. Phys. Lett.*, **56**, 1734 (1990).

10 B. F. Levine and C. G. Bethea, *Appl. Phys. Lett.*, **24**, 445 (1974); J. L. Oudar and H. L. Person, *Opt. Commun.*, **15**, 258 (1975); K. D. Singer and A. F. Garito, *J. Chem. Phys.*, **75**, 3572 (1981); L. -T. Cheng, W. Tam, S. H. Stevenson, G. R. Meredith, G. Rikken, and S. R. Marder, *J. Phys. Chem.*, **95**, 10631 (1991).

11 J. L. Ouder and D. S. Chemla, *J. Chem. Phys.*, **66**, 2664 (1977); J. L. Order, *J. Chem. Phys.*, **67**, 446 (1977).