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Synthesis and Nonlinear Optical Properties of Donor–Acceptor Substituted Triaryl Azole Derivatives

Christopher R. Moylan, Robert D. Miller, Robert J. Twieg, Kathleen M. Betterton, Victor Y. Lee, Tracy J. Matray, and Cattien Nguyen

IBM Almaden Research Center, 650 Harry Road, San Jose, California 95120-6099

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A variety of optically nonlinear chromophores containing a five-membered imidazole, oxazole, or thiazole ring have been prepared and characterized. These consist of 2,4,5-triphenyl-substituted azole heterocyclic systems in which the 2-aryl ring bears an electron-withdrawing substituent and the 4,5-aryl rings bear an electron-donating substituent. Additionally, some planar analogues, phenanthro[9,10-*d*]imidazoles, were also prepared and evaluated. The utility of these chromophores will be dictated by their linear absorption wavelength and oscillator strength, microscopic optical nonlinearity, ground-state dipole moment, thermal stability, and solubility. The tradeoffs between these structure-dependent properties are discussed with regard to exploitation of these chromophores as guest dyes in high-temperature thermoplastics.

Introduction

One of the outstanding problems that must be solved prior to practical technological application of organic polymeric nonlinear optical materials[1,2] is the preparation of thermally stable, oriented materials in which full advantage is taken of large molecular hyperpolarizabilities to yield large bulk material susceptibilities. For this reason, the search for nonlinear chromophores is not simply a quest to find the molecule with the highest value of the microscopic hyperpolarizability β. Practical applications in integrated electrooptical devices place numerous demands on the chromophore other than just appreciable nonlinearity. For example, a high-frequency electrooptical switch or phase or amplitude modulator integrated into an appropriate semiconductor device may operate continually at temperatures in excess of 80 °C and may experience brief excursions to 250 °C or more in the fabrication process.[3] Therefore, the polymer–chromophore system must be thermally stable, maintain polar order, retain homogeneity and good linear optical properties, and not degrade under other environmental influences.

Due to thermal stability concerns, significant effort has been devoted to the study of NLO chromophores containing six-membered aromatic rings (benzene and its linear and polynuclear derivatives) and six-membered heteroaromatic rings (pyridine, pyrimidine, etc., and their various linear combinations and polynuclear derivatives).[4,5] These chromophores have been used in a wide variety of poled polymer systems.[6] Much less effort, however, has been expended in the area of five-membered heterocyclic azole derivatives such as imidazoles, oxazoles, thiazoles, and pyrazoles, even though the utility of heterocyclic ring systems in nonlinear organic molecules has been suggested.[7] For example, Dirk and co-workers[8,9] and others[10,11] have found that 2,5-disubstituted thiazole derivatives have potential for nonlinear applications. We have shown that substituted pyrazoles are promising nonlinear chromophores as well.[12] Like the six-membered ring systems, these stable heterocycles can provide a fully conjugated planar framework for the attachment of appropriate substituent groups, and they possess impressive thermal and oxidative stabilities. The use of five-membered-ring heterocycles also provides a significant synthetic advantage, because the chromophores are often prepared using a one-step formation of the heterocyclic ring. Such synthetic flexibility contrasts vividly with the situation involving six-membered ring systems, especially those containing only benzene rings, where the preparation is usually limited to linking preformed benzene-containing units together.

We report here the synthesis and nonlinear optical characterization of a variety of triaryl azole chromophores (Figure 1) including triaryl substituted imidazole **1**, oxazole **2**, and thiazole **3** derivatives, as well as planarized imidazole derivatives, phenanthro[9,10-*d*]imidazoles **4**. These chromophores constitute a particularly stable class of five-membered ring-containing heterocycles. We have also performed geometry minimization calculations on model compounds and relate the results to our experimental data. Not only do these chromophores exhibit substantial

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(1) Chemla, D. S., Zyss, J., Eds. *Nonlinear Optical Properties of Organic Molecules and Crystals*; Academic Press: New York, 1987; Vols. 1 and 2.

(2) Prasad, P. N.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; Wiley: New York, 1991.

(3) Lipscomb, G. F.; Lytel, R. S.; Ticknor, A. J.; Van Eck, T. E.; Kwiatkowski, S. L.; Girton, D. G. *Proc. SPIE* **1990**, *1337*, 23.

(4) Nicoud, J. F.; Twieg, R. J. In ref 1, Vol. 1, p 227 and Vol. 2, p 221.

(5) Cheng, L.-T.; Tam, W.; Stevenson, S. H.; Meredith, G. R.; Rikken, G.; Marder, S. R. *J. Phys. Chem.* **1991**, *95*, 10631; *Ibid*, 10643.

(6) Lee, K.-S.; Samoc, M.; Prasad, P. N. In *Comprehensive Polymer Science (First Supplement)*; Allen, G. A., Aggarwal, S. L., Saverio, R., Eds.; Pergamon Press: Oxford, 1992; pp 407–447.

(7) Twieg, R. J.; Jain, K. In *Nonlinear Optical Properties of Organic and Polymeric Materials*; Williams, D. J., Ed.; ACS Symposium Series 233; American Chemical Society: Washington, DC, 1984; pp 57–80.

(8) Dirk, C. W.; Katz, H. E.; Schilling, M. L.; King, L. A. *Chem. Mater.* **1990**, *2*, 700.

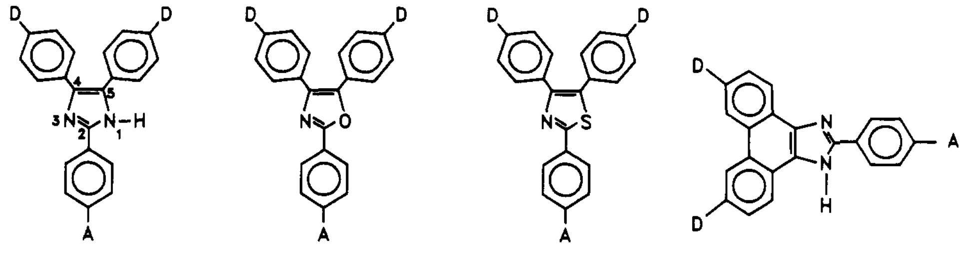
(9) Dirk, C. W.; King, L.; Katz, H. In *Nonlinear Optical Materials*, Kuhn, H., Robillard, V., Eds.; CRC Press: Boca Raton, FL, 1992; p 203.

(10) Okazaki, M.; Kubodem, S.; Minamirashigora, K. German Patent DE3737456A1, 1988.

(11) Miller, R. D.; Moylan, C. R.; Reiser, O.; Walsh, C. A., unpublished results.

(12) Miller, R. D.; Moylan, C. R.; Reiser, O.; Walsh, C. A. *Chem. Mater.* **1993**, *5*, 625.

0897-4756/93/2805-1499$04.00/0



1a–i,k **2a–c,j–n** **3a,e** **4a,e,f,k**

	D	A		D	A
a.	CH_3O	NO_2	h.	CH_3OPhS	NO_2
b.	CH_3O	$O_2NPhC{\equiv}C-$	i.	$c-(CH_2)_6N$	NO_2
c.	CH_3O	SO_2Ph	j.	CH_3O	C_6F_{13}
d.	$c-(CH_2)_5N$	NO_2	k.	CH_3O	$SO_2C_4F_9$
e.	$C_4H_9CH(C_2H_5)CH_2O$	NO_2	l.	CH_3O	CF_3
f.	$C_4H_9CH(C_2H_5)CH_2O$	$SO_2C_4F_9$	m.	CH_3O	SO_2CH_3
g.	$CH_3OPhC{\equiv}C-$	NO_2	n.	CH_3O	SO_2PhCF_3

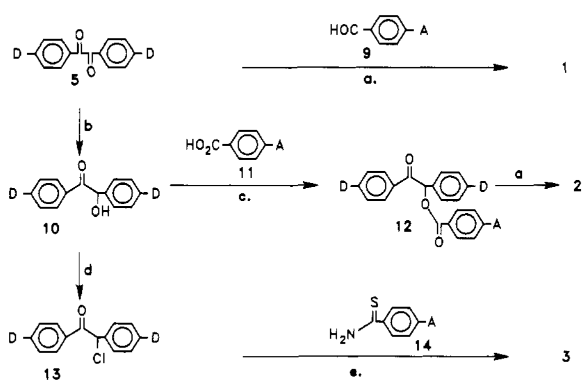
Figure 1. Molecular structures of the heterocyclic compounds characterized in this work.

nonlinearity and thermal stability, but they can be used effectively in simple host-guest polymer systems[13–15] without requiring cross-linking[16–19] or incorporation into polymers either as side groups or in the backbone.[20–22] Recent studies of some simple donor-acceptor substituted triarylimidazoles in polyimide hosts have demonstrated that these NLO chromophores show excellent solubility, compatibility, and useful thermal stability and maintain significant polar order even at elevated temperatures.[23,24]

Experimental Section

Synthesis. All the triphenylazoles **1–3** substituted with donor (D) and acceptor (A) groups were prepared by standard cyclocondensation reactions. The general approach is summarized in Scheme I. In the case of the 2,4,5-triphenylimidazoles (lophines) **1**, the synthesis involves condensation of a benzil **5** bearing electron-donating groups on the 4,4′-positions with an aldehyde **9** bearing an electron-withdrawing group in the 4-position with ammonium acetate in acetic acid.[25] The 2,4,5-triphenyloxazoles **2** were prepared by ring closure of a benzoin benzoate ester **12** with ammonium acetate in acetic acid.[25] Here the benzoate bears an electron-withdrawing group at the 4-position and the electron donating groups reside on the 4,4′-positions of the benzoin part of ester **12**. The benzoin benzoates were prepared by (dimethylamino)pyridine (DMAP) catalyzed dicyclohexylcarbodiimide (DCC) coupling of the requisite substituted benzoin **10** and benzoic acid **11** partners. Many simple 4,4′-substituted benzoins **10** are commercially available. Others can be synthesized by a wide variety of techniques involving reduction of the appropriate benzil[26] or by benzoin condensation of the appropriate benzaldehyde.[27] The 2,4,5-triphenylthiazole **3a** was prepared by reaction of α-chlorodesoxyanisoin (**13**, D = OMe) prepared from anisoin (**10**, D = OMe) and thionyl chloride by a modification of a literature method,[28] with 4-nitrothiobenzamide **14**, itself prepared from the amide with Lawesson's reagent.[29] (Perfluorobutyl)sulfonyl benzaldehyde (**9**, A = $SO_2(CF_2)_4F$) was prepared by hydrolysis of the ethylene acetal of 4-(perfluorobutylsulfonyl)benzaldehyde **8**, which was in turn prepared from the ethylene acetal of bromobenzaldehyde **7**. (Perfluorobutyl)sulfonyl benzoic acid (**11**, A = $SO_2(CF_2)_4F$) was prepared by a multistep procedure beginning with 4-mercaptobenzoic acid[30] or, better, by oxidation of the aldehyde **9**.

Scheme I



[a] NH_4OAc (3–5 equiv), HOAc, Δ. [b] Zn (5–10 equiv), DMF, H_2O, Δ. [c] Dicyclohexylcarbodiimide (DCC), (dimethylamino)pyridine (DMAP, catalytic), CH_2Cl_2. [d] $SoCl_2$, pyridine, CH_2Cl_2. [e] NaOAc, HOAc, Δ.

The planarized phenanthro[9,10-*d*]imidazoles **4a,e,f,k** were prepared by the multistep sequence shown in Scheme II. The

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(13) Singer, K. D.; Sohn, J. E.; Lalama, S. J. *Appl. Phys. Lett.* **1986**, *49*, 248.

(14) Wu, J. W.; Valley, J. F.; Ermer, S.; Binkley, E. S.; Kenney, J. T.; Lipscomb, G. F.; Lytel, R. *Appl. Phys. Lett.* **1991**, *58*, 225.

(15) Valley, J. F.; Wu, J. W.; Ermer, S.; Stiller, M.; Binkley, E. S.; Kenney, J. T.; Lipscomb, G. F.; Lytel, R. *Appl. Phys. Lett.* **1992**, *60*, 160.

(16) Reck, B.; Eich, M.; Jungbauer, D.; Twieg, R. J.; Willson, C. G.; Yoon, D. Y.; Bjorklund, G. C. *Proc. SPIE* **1989**, *1147*, 74.

(17) Eich, M.; Bjorklund, G. C.; Yoon, D. Y. *Polym. Adv. Technol.* **1990**, *1*, 189.

(18) Mandal, B. K.; Chen, Y. M.; Lee, J. Y.; Kumar, J.; Tripathy, S. *Appl. Phys. Lett.* **1991**, *58*, 2459.

(19) Chen, M.; Yu, L.; Dalton, L. R.; Shi, Y.; Steir, W. H.*Macromolecules* **1991**, *24*, 5421.

(20) Singer, K. D.; Lalama, S. J.; Sohn, J. E. *SPIE Int. Opt. Circuit Eng. II* **1985**, *578*, 130.

(21) Willand, C. S.; Feth, S. E.; Scozzafava, M.; Williams, D. J.; Green, G. D.; Weinschenk, J. I.; Hall, H. K.; Mulvaney, J. E. In *Nonlinear Optical and Electroactive Polymers*; Prasad, P. N., Ulrich, D. R., Eds.; Plenum Press: New York, 1988; p 107.

(22) Man, H.-T.; Yoon, H. N. *Adv. Mater.* **1992**, *4*, 159.

(23) Stähelin, M.; Burland, D. M.; Ebert, M.; Miller, R. D.; Smith, B. A.; Twieg, R. J.; Volksen, W.; Walsh, C. A. *Appl. Phys. Lett.* **1992**, *61*, 1626.

(24) Stähelin, M.; Walsh, C. A.; Burland, D. M.; Miller, R. D.; Twieg, R. J.; Volksen, W. *J. Appl. Phys.* **1993**, *73*, 8471.

(25) Davidson, D.; Weiss, M.; Jelling, M. J. *J. Org. Chem.* **1937**, *2*, 319.

(26) Kreiser, W. *Liebigs Ann. Chem.* **1971**, *745*, 164.

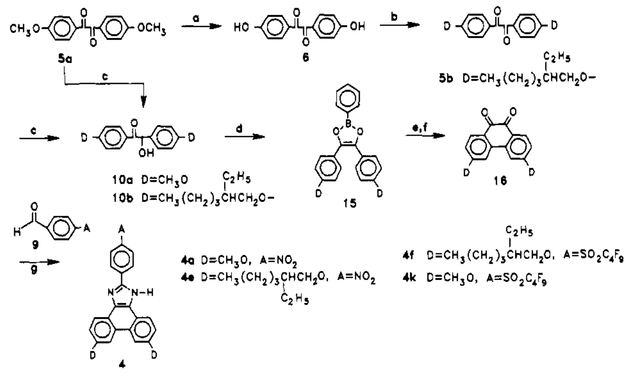
(27) Ide, W. S.; Buck, J. S. In *Organic Reactions*; Adams, R., Ed.; John Wiley: New York, 1948; Vol. IV, pp 269–304.

(28) Henne, G.; Bruylants, A. *Rec. Trav. Chim. Pays-Bas* **1960**, *57*, 1948.

(29) Scheibye, S.; Pederson, B. S.; Lawesson, S.-O. *Rec. Trav. Chim. Pays-Bas.* **1978**, *87*, 229.

(30) Twieg, R. J.; unpublished results.

Scheme II



[a] 48% HBr, HOAc, Δ. [b] $CH_3(CH_2)_3CH(C_2H_5)CH_2Br$, Bu_4NBr, K_2CO_3. [c] Zn, DMF, H_2O, 120 °C. [d] $PhB(OH)_2$, benzene, carbonyl diimidazole, Δ. [e] *hν*, $(PhSe)_2$, 450-W Hg lamp. [f] 1 M NaOH. [g] NH_4OAc, HOAc, Δ.

4,4′-alkoxy substituted benzoins are conveniently prepared from anisil **5a** which is first dealkylated with HBr. The resulting 4,4′-dihydroxybenzil **6** can then be easily alkylated to provide a variety of other alkoxy donor groups, e.g., **5b**. These benzils are readily reduced by zinc to alkoxy-substituted benzoins such as **10b**. The donor-substituted benzoins **10a,b** were subsequently converted to the 2,4,5-triphenyl-1,3-dioxaboroles **15** with phenylboronic acid[31] and carbonyl diimidazole, which were photocyclized in the presence of diphenyl diselenide[32] and the mixture hydrolyzed. The desired 3,6-dialkoxy-9,10-phenanthroquinones **16** are easily isolated by chromatography. Just as in the case of the benzil derivatives, the reaction of substituted 9,10-phenanthroquinones with benzaldehyde derivatives and ammonium acetate in acetic acid produces the imidazole heterocycles,[33] 3,6-disubstituted 2-phenylphenanthro[9,10-*d*]imidazoles **4a,e,f,k**, in good yield. In the reaction of the phenanthroquinone **16b** with **9** (A = $SO_2C_4F_9$) the corresponding oxazole **17** is produced concurrently.

Representative detailed experimental procedures for each of the general classes of chromophores are provided below.

2-(4′-Nitrophenyl)-4,5-(4′-methoxyphenyl)imidazole (**1a**). In a 1-L round-bottom flask equipped with a stir bar, reflux condenser, and nitrogen bubbler was placed 4-nitrobenzaldehyde (**9**, A = NO_2, 7.60 g, 50 mmol), 4,4′-dimethoxybenzil (**5a**, D = OMe, 13.5 g, 50 mmol), ammonium acetate (38.6 g, 500 mmol), and acetic acid (300 mL). The resulting solution was refluxed and gradually became orange over 6h. The mixture was cooled to room temperature and water (500 mL) was added dropwise. The orange solid was collected by suction filtration, washed with water, and then recrystallized from aqueous acetic acid. The recrystallized product (22.7 g, 91%, containing approximately one molecule of acetic acid and two molecules of water per molecule of product as co-crystallites) was isolated by suction filtration, washed well with water, and air dried in the filter and then in a vacuum oven overnight at room temperature: mp 104–107 °C [lit.[34] mp 98 °C], ^{1}H NMR ($CDCl_3$) δ 8.12 (d, *J* = 9Hz, 2H), 7.96 (d, *J* = 9Hz, 2H), 7.35 (d, *J* = 9 Hz, 2H), 6.85 (d, *J* = 9Hz, 2H), 5.85–6.10 (br s, ≃4.5H), 3.82 (2, 3H), 2.06 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 178.84, 159.18, 147.00, 142.83, 135.20, 133.66, 129.02, 125.34, 124.26, 124.14, 114.00, 55.18, 20.72.

The solvent of recrystallization is readily removed by heating above the melting point under vacuum. The solvent-free product so obtained is a red solid with mp 217–220 °C [lit.[34] mp 220–221 °C], ^{1}H NMR ($CDCl_3$) δ 8.14–8.20 (m, 2H), 7.92–7.97 (m, 2H), 7.41 (br d, *J* = 9Hz, 2H), 6.83–6.88, (m, 2H), 3.81 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 159.15, 146.94, 142.96, 135.46, 129.02, 125.27, 142.11, 113.99, 55.18.

1,2-Bis(4′-methoxyphenyl)-2-hydroxyethanone 4-Nitrobenzoate Ester (**12**, *D = OMe, A = NO_2*). In a 500-mL round-bottom flask equipped with a stir bar and nitrogen bubbler was placed anisoin (**10**, D = OMe, 5.44 g, 20 mmol), 4-nitrobenzoic acid (**11**, A = NO_2, 3.34 g, 20 mmol), 4-(dimethylamino)pyridine (100 mg), and dichloromethane (75 mL). The resulting suspension was stirred and dicyclohexylcarbodiimide (4.53 g, 22 mmol) was added in one portion. After this was stirred for 4 h, silica gel was added to the mixture and it was concentrated to dryness. This material was placed at the top of a silica gel column and eluted with a gradient of ethyl acetate in hexane (10% → 30%). Fractions containing pure product were combined, concentrated, and recrystallized from ethanol to give a white crystalline solid (7.90g, 93%): mp 114–117 °C [lit.[35] mp 121–122 °C]; ^{1}H NMR ($CDCl_3$) δ 8.28 (s, 4H), 7.97 (d, *J* = 9Hz, 2H), 7.48 (d, *J* = 9Hz, 2H), 7.06 (s, 1H), 6.88–6.06 (m, 4H), 3.84 (s, 3H), 3.81 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 191.17, 164.16, 163.78, 160.45, 150.55, 134.97, 131.10, 130.98, 130.23, 127.07, 125.43, 123.40, 114.61, 113.87, 78.16, 55.38, 55.21. Anal. Calcd for $C_{23}H_{19}NO_7$: C, 65.56; H, 4.54; N, 3.32. Found: C, 65.38; H, 4.64; N, 3.34.

2-(4′-Nitrophenyl)-4,5-(4′-methoxyphenyl)oxazole (**2a**). Into a 200-mL pear-shaped flask equipped with a stir bar, reflux condenser and nitrogen inlet was placed the anisoin nitrobenzoate (**12**, D = OMe, A = NO_2, 3.00 g, 7.1 mmol), ammonium acetate (3.28 g, 42.6 mmol), and acetic acid (30 mL). The resulting mixture was maintained at a gentle reflux for 2 h, then cooled, and diluted to 200 mL by the dropwise addition of water. The resulting solid was isolated by suction filtration, washed with water, air dried, and recrystallized twice from aqueous acetic acid to give the product (2.12 g, 74%) as yellow crystals: mp K 186 K 205–209 °C, ^{1}H NMR ($CDCl_3$) δ 8.26–8.37 (m, 4H), 7.60–7.67 (m, 4H), 6.92–6.98 (m, 4H), 3.87 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 160.06, 159.61, 157.23, 148.25, 146.48, 136.26, 132.83, 129.15, 128.14, 126.71, 124.35, 124.00, 120.89, 114.18, 114.04, 55.26, 55.23. Anal. Calcd for $C_{23}H_{18}N_2O_5$: C, 68.65; H, 4.51; N, 6.96. Found: C, 68.94; H, 4.73; N, 6.94.

4,5-Bis(4′-methoxyphenyl)-2-(4′-nitrophenyl)thiazole (**3a**). A solution of 1,2-bis(4′-methoxyphenyl)-1-chloroethan-2-one (**13**, D = OMe, 0.35 g, 1.2 mmol), 4-nitrothiobenzamide (**14**, A = NO_2, 0.22 g, 1.2 mmol), and sodium acetate (0.1 g, 1.2 mmol) were heated to reflux in 10 mL acetic acid for 3 h. The reaction mixture was diluted with water and the yellow precipitate was filtered. Purification by flash chromatography[36] on silica gel with 20% acetone–hexane and recrystallization from ethanol gave 0.40 g (76%) of yellow crystals: mp 144–146 °C; ^{1}H NMR ($CDCl_3$) δ 8.30 (d, *J* = 8.8 Hz, 2H), 8.15 (d, *J* = 8.8 Hz, 2H), 7.55 (d, *J* = 8.8 Hz, 2H), 7.34 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 3.83 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 161.3, 159.7, 159.4, 151.1, 148.0, 139.2, 134.2, 130.7, 130.2, 127.0, 126.6, 124.2, 123.6, 114.2, 113.7, 55.22, 55.16; IR (KBr) 3001–2912, 2840, 1609, 1599, 1521, 1483, 1141, 1346, 1250, 1179, 1109, 1034, 988, 854, 832, 752, 691, 579 cm^{-1}.

2-(4′-Bromophenyl)-1,3-dioxolane (**7**). A 500-mL flask equipped with a Dean–Stark condenser was charged with 18.5 g (0.1 mol) of 4-bromobenzaldehyde, 7.1 g (0.11 mol) of ethylene glycol, 0.2 g of *p*-toluenesulfonic acid hydrate, and 320 mL of benzene. The solution was refluxed under nitrogen for 8 h. The resulting mixture was diluted with ether and extracted with dilute aqueous sodium bicarbonate. The organic phase was dried over sodium sulfate and concentrated. The crude product was vacuum distilled at 80 °C, 20 mTorr. The clear liquid was redistilled from lithium aluminum hydride in a 100-mL flask. After the initial foaming had subsided, the product was distilled at 76–78 °C, 25 mTorr to give 21.0 g (91% yield) clear liquid which solidified on standing: mp 31–34 °C; ^{1}H NMR δ ($CDCl_3$), 7.52 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 6.11 (s, 1H), 4.15–3.97 (m, 4H); ^{13}C NMR δ ($CDCl_3$), 136.9, 132.3, 131.4, 130.9, 128.1, 123.1, 102.9, 65.2; IR ($CDCl_3$) 2956, 2890, 1596, 1486, 1420, 1381, 1347, 1298, 1217, 1108, 1080, 1028, 1013, 973, 944, 819, 522 cm^{-1}.

2-(4′-(Perfluorobutyl)sulfonylphenyl)-1,3-dioxolane (**8**). Magnesium turnings (0.42 g, 17.5 mmol) were dried under vacuum at 80 °C overnight. After this cooled to room temperature, 10 mL of dry THF and a few crystals of iodine was added to the mixture. A solution of 2-(4′-bromophenyl)-1,3-dioxolane (4.0 g,

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(31) Letsinger, R. L.; Hamilton, S. B. *J. Org. Chem.* **1960**, *25*, 592.

(32) deVries, J. G.; Hubbard, S. A. *J. Chem. Soc., Chem. Commun.* **1988**, 1172.

(33) Steck, E. A.; Day, A. R. *J. Am. Chem. Soc.* **1943**, *65*, 452.

(34) Sakaino, Y.; Takizawa, T.; Inouye, Y.; Kakisawa, H. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1623.

(35) Strzbny, P. P. E.; Van Es, T.; Backeberg, O. G. *J. S. Afr. Chem. Inst.* **1969**, *22*, 158; CA 72:43563q.

(36) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

17.5 mmol) in 40 mL of THF was added dropwise to the magnesium mixture with efficient stirring. The rate of addition was varied to maintain the reaction temperature at 30–35 °C. The light brown solution was stirred for 3 h at 30 °C. The Grignard reagent was cannulated into a solution of (perfluorobutyl)sulfonyl fluoride (5.3 g, 17.5 mmol) in 40 mL of THF at −40 °C. The reaction was allowed to warm to room temperature overnight. The mixture was poured into aqueous ammonium chloride and extracted with portions of ether. The organic phases were combined, dried over sodium sulfate, and concentrated under reduced pressure. The crude residue was chromatographed on silica gel with 20% ethyl acetate–hexanes and after recrystallization from carbon tetrachloride gave a white solid (2.1 g, 28% yield): mp 59–60 °C; ^{1}H NMR δ ($CDCl_3$), 8.06 (d, J = 8.4 Hz, 2H), 7.79 (d, J = 8.5 Hz, 2H), 5.93 (s, 1H), 4.17–4.06 (m, 4H); ^{13}C NMR δ ($CDCl_3$), 147.2, 132.4, 131.1, 127.6, 101.9, 65.4; IR ($CDCl_3$) 2975, 2882, 1369, 1351, 1240, 1211, 1206, 1187, 1172, 1142, 1122, 1080, 1029, 1016, 1006, 584 cm^{-1}.

4-(Perfluorobutyl)sulfonylbenzaldehyde (***9***, *A* = $SO_2C_4F_9$). 2-(4′-(Perfluorobutyl)sulfonylphenyl)-1,3-dioxolane **8** (0.5 g, 1.16 mmol) dissolved in 40 mL of THF was stirred with 50 mL 3 M sulfuric acid for 1 h at 70 °C. The mixture was diluted with water, neutralized with sodium bicarbonate, and extracted with portions of ether. The combined organic layers were dried over sodium sulfate, the solvent removed under vacuum, and the residual oil was chromatographed on silica gel with 20% ethyl acetate–hexane. Recrystallization from petroleum ether gave white platelets (0.37 g, 82% yield): mp 78–79 °C; ^{1}H NMR δ ($CDCl_3$), 10.20 (s, 1H), 8.25 (d, J = 8.4 Hz, 2H), 8.18 (d, J = 8.4 Hz, 2H); ^{13}C NMR δ ($CDCl_3$), 190.1, 141.3, 136.9, 131.8, 130.2; IR ($CDCl_3$) 1715, 1375, 1351, 1290, 1241, 1218, 1201, 1178, 1142, 1121, 1080, 826, 582 cm^{-1}. Anal. Calcd for $C_{11}H_5F_9O_3S$: C, 34.03; H, 1.30; F, 44.04; S, 8.26. Found: C, 33.70; H, 1.39; F, 43.93; S, 8.34.

4,4′-Dihydroxybenzil (***6***). A suspension of 4,4′-dimethoxybenzil (**5**, D = OMe, 1.5 g, 5.5 mmol) in 15 mL of acetic acid and 60 mL of HBr (48% aqueous) was heated to reflux for 4 h. The homogeneous mixture was cooled and diluted with 200 mL of water. The precipitate was filtered, washed with water, and dried to give 1.1 g (82%) of a light tan solid: mp 250–255 °C [lit.[37] mp 244–246 °C]; ^{1}H NMR (acetone-d_6) δ 9.58 (s, 1H), 7.83 (d, J = 8.8 Hz, 4H), 6.99 (d, J = 8.88 Hz, 4H); ^{13}C NMR (acetone-d_6) δ 194.3, 164.1, 132.9, 126.1, 116.6; IR (KBr) 3409, 1644, 1600, 1579, 1513, 1368, 1319, 1292, 1225, 1175, 880, 849, 809, 770, 755, 706, 640, 602, 515, 452 cm^{-1}.

4,4′-Bis(2-ethylhexyloxy)benzil (***5b***, *D = 2-Ethylhexyloxy*). A mixture of 2.0 g (8.26 mmol) of 4,4′-dihydroxybenzil **6**, 3.51 g (18.2 mmol) of 2-ethylhexylbromide, 1.33 g (4.1 mmol) of tetrabutylammonium bromide, and 2.40 g (17.3 mmol) of potassium carbonate were stirred in 60 mL of dimethylformamide at 100–120 °C for 1.5 h. The reaction mixture was diluted with aqueous NaCl and extracted with three 60-mL portions of ether. The combined organic extracts were washed with water, dried over sodium sulfate, and filtered, and solvents removed under vacuum. The crude product was chromatographed on silica gel with 5% acetone in hexanes to give 2.9 g (75%) of a light yellow colored oil: ^{1}H NMR δ ($CDCl_3$) 7.93 (d, J = 8.9 Hz, 4H), 6.96 (d, J = 9.0 Hz, 4H), 3.92 (d, J = 5.7 Hz, 4H), 1.77–1.70 (m, 2H), 1.54–1.40 (m, 8H), 1.33–1.27 (m, 8H), 0.96–0.88 (m, 12H); ^{13}C NMR δ ($CDCl_3$) 193.5, 164.6, 132.2, 125.9, 114.6, 70.8, 39.1, 30.3, 28.9, 23.6, 22.9, 13.9, 10.9; IR (KBr) 2962, 2932, 2875, 2861, 1668, 1597, 1572, 1510, 1464, 1425, 1309, 1264, 1229, 1176, 1161, 1023, 881, 844, 618 cm^{-1}. High-resolution mass spectrum calcd for $C_{30}H_{42}O_4$: 466.3083. Found: 466.3078.

2-(4′-Nitrophenyl)-4,5-bis(4-(2′-ethylhexyloxy)phenyl)imidazole (***1e***). A solution containing 2.0 g (4.29 mmol) of 4,4′-bis(2-ethylhexyloxy)benzil (**5b**), 0.78 g (5.15 mmol) of *p*-nitrobenzaldehyde, and 6.6 g (86 mmol) of ammonium acetate in 50 mL of acetic acid were heated to reflux for 4 h. The homogeneous solution was poured into ice water to give a tacky red solid. The mixture was filtered through a pad of Celite, rinsed well with water, and dried. The crude product was dissolved in hot ethyl acetate, filtered, and chromatographed on silica gel with 15% acetone in hexanes to yield 2.4 g (92%) of a viscous red oil which solidified upon storage under vaccum: mp 60–62 °C; ^{1}H NMR δ (THF-d_8) 11.7 (s, 1H), 8.16 (d, J = 7.0 Hz, 2H), 8.08 (d, J = 6.9 Hz, 2H), 7.45 (d, J = 8.7 Hz, 2H), 7.30 (d, J = 8.7 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H), 6.70 (d, J = 8.7 Hz, 2H), 3.80 (d, J = 5.6 Hz, 2H), 3.75 (d, J = 5.5 Hz, 2H), 1.65–1.55 (m, 2H), 1.44–1.31 (m, 8H), 1.29–1.19 (m, 8H), 0.87–0.76 (m, 12H); ^{13}C NMR δ (THF-d_8) 160.3, 159.3, 147.8, 143.8, 139.7, 137.6, 130.5, 129.9, 129.2, 128.5, 125.9, 124.7, 124.5, 115.3, 114.6, 71.0, 70.8, 40.5, 31.5, 30.0, 24.6, 23.9, 14.4, 11.4; IR ($CDCl_3$) 3447, 2962, 2931, 2874, 2862, 1615, 1603, 1518, 1494, 1464, 1340, 1291, 1249, 1176, 1111, 855, 835 cm^{-1}. Anal. Calcd for $C_{37}H_{47}N_3O_4$: C, 74.34; H, 7.92; N, 7.03. Found: C, 74.51; H, 8.11; N, 7.14.

4,4′-Bis(2′-ethylhexyloxy)benzoin (***10b***, *D = 2-Ethylhexyloxy*). Zinc dust (2.89 g, 44 mmol) was added to a solution containing 3.45 g (7.4 mmol) of 4,4′-bis(2-ethylhexyloxy)benzil **5b** in 90 mL DMF and 30 mL of water with vigorous stirring. After the mixture was heated to reflux for 3 h, the cooled suspension was filtered and washed with 300 mL of ether. The filtrate was extracted with aqueous NaCl and the organic layer was dried over sodium sulfate. After the solvent was removed under reduced pressure, the oily residue was purified by column chromatography on silica gel with 10% acetone in hexanes to give a clear viscous oil (3.3 g, 95% yield): ^{1}H NMR δ (THF-d_8) 7.96 (d, J = 8.9 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 6.90 (d, J = 8.9 Hz, 2H), 6.81 (d, J = 8.0 Hz, 2H), 5.86 (d, J = 6.5 Hz, 1H), 4.88 (dd, J = 2.3 Hz, J = 6.5 Hz, 1H), 3.91 (d, J = 5.5 Hz, 2H), 3.81 (d, J = 5.5 Hz, 2H), 1.69–1.63 (m, 2H), 1.54–1.42 (m, 8H), 1.39–1.34 (m, 8H) 0.96–0.88 (m, 12H); ^{13}C NMR δ ($CDCl_3$) 197.2, 163.7, 159.3, 131.4 (2C), 128.8, 125.9, 114.9, 114.2, 75.1, 70.6, 70.3, 39.2, 39.1, 30.4, 30.3, 28.92, 28.89, 23.68, 23.63, 22.90, 22.88, 13.9 (2C), 10.9 (2C); IR ($CDCl_3$) 3467, 2962, 2931, 2875, 2861, 1667, 1600, 1572, 1512, 1465, 1382, 1308, 1256, 1172, 1073, 1030, 976, 832, 587 cm^{-1}.

3,6-Bis(2-ethylhexyloxy)-9,10-phenanthrenedione (***16***, *D = 2-Ethylhexyloxy*). A mixture containing 2.0 g (4.27 mmol) of 4,4′-bis(2-ethylhexyloxy)benzoin (**10b**), 0.52 g (4.27 mmol) of phenylboronic acid, and 0.7 g (4.27 mmol) of carbonyl diimidazole in 180 mL of benzene was refluxed for 2.0 h under an inert atmosphere. The cooled solution was cannulated into a 1-L photochemical reaction vessel containing a degassed solution of 2.67 g (8.55 mmol) of diphenyl diselenide dissolved in 800 mL of benzene. The solution was purged continuously with argon and irradiated with a medium-pressure mercury lamp through a Pyrex filter sleeve for 12 h. The reaction mixture was hydrolyzed by stirring vigorously with 200 mL of 1 M NaOH in air for 60 min. The organic phase was separated, washed with water, dried over sodium sulfate, and concentrated under reduced pressure. The residue was chromatographed on silica gel with 10% ethyl acetate in hexanes to give diphenyl diselenide (1.8 g, 67% recovery) and a light-yellow viscous oil (1.3 g, 65% yield): ^{1}H NMR δ ($CDCl_3$) 8.18 (d, J = 8.75 Hz, 2H), 7.38 (d, J = 2.3 Hz, 2H), 6.94 (dd, J = 2.25 Hz, 1H, J = 8.75 Hz, 1H), 4.02 (d, J = 5.55 Hz, 4H), 1.82–1.75 (m, 2H), 1.57–1.32 (m, 16H), 1.00–0.90 (m, 12H); ^{13}C NMR δ ($CDCl_3$) 179.0, 165.4, 137.6, 133.2, 124.9, 114.5, 110.3, 71.0, 39.2, 30.3, 29.0, 23.6, 22.9, 14.0, 11.0; IR (KBr) 2959, 2931, 2873, 2861, 1672, 1599, 1563, 1497, 1465, 1343, 1321, 1243, 1197, 1130, 1033, 1012, 926, 870, 850, 825, 737 cm^{-1}.

2-(4′-Nitrophenyl)-6,9-bis(2′-ethylhexyloxy)-1H-phenanthro[9,10-d]imidazole (***4e***). A mixture containing 0.38 g (0.82 mmol) of 3,6-bis(2-ethylhexyloxy)-9,10-phenanthrenedione (**16**), 0.15 g (1.0 mmol) of 4-nitrobenzaldehyde, 1.23 g (16 mmol) of ammonium acetate, and 25 mL of acetic acid was heated to reflux for 4 h. After cooling, the red solution was poured into ice water. The resulting orange solid was collected by filtration, washed, and dried. The crude product was chromatographed on silica gel with 15% acetone in hexanes and recrystallized from ethanol to give red crystals (1.1 g, 62% yield): mp 171–172 °C; ^{1}H NMR δ (THF-d_8) 12.42 (s, 1H), 8.59 (d, J = 8.7 Hz, 1H), 8.34 (d, J = 8.9 Hz, 2H), 8.30 (d, J = 8.9 Hz, 2H), 8.13 (d, J = 9.4 Hz, 3H), 7.34 (t, J = 8.3 Hz, 2H), 4.14 (d, J = 3.7 Hz, 4H), 1.85–1.83 (m, 2H), 1.70–1.57 (m, 8H), 1.50–1.40 (m, 8H), 1.06–0.94 (m, 12H); ^{13}C NMR δ (THF-d_8) 158.54, 158.46, 148.2, 146.6, 138.4, 137.6, 131.1, 130.2, 128.5, 126.7, 124.7, 124.6, 123.5, 123.0, 118.0, 117.0, 116.9, 108.4, 107.9, 71.1, 40.7, 31.6, 30.1, 24.6, 23.9, 14.4, 11.6; IR ($CDCl_3$) 3462, 2962, 2931, 2874, 2862, 1625, 1602, 1549, 1518, 1464, 1442, 1414, 1340, 1325, 1235, 1183, 1100, 1064, 1030, 855

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(37) Schonberg, A.; Kramer, O. *Chem. Ber.* **1922**, *55*, 1174.

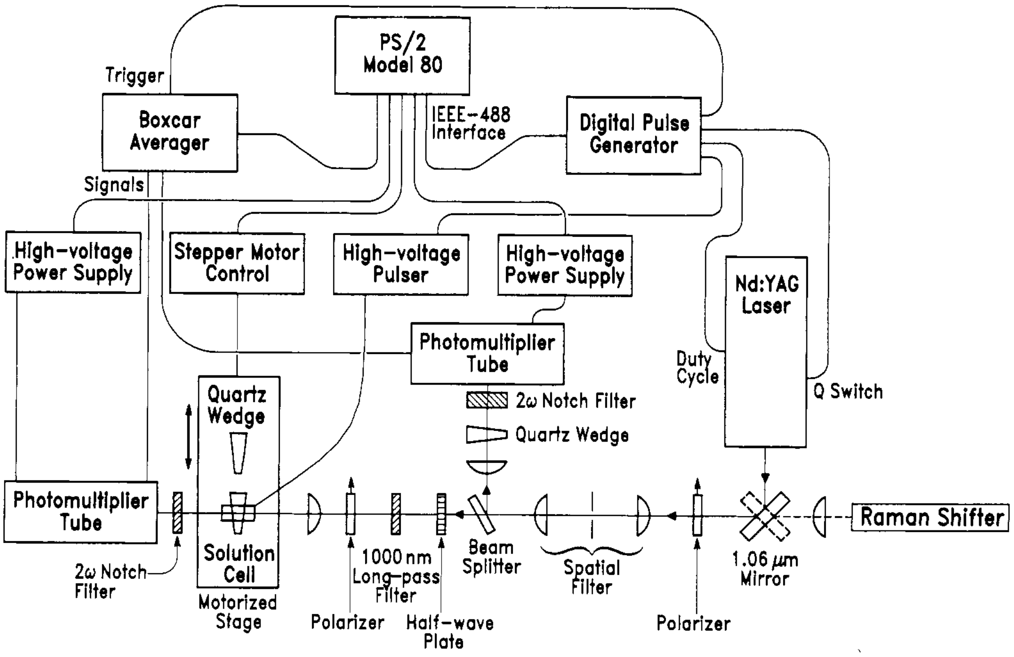

Figure 2. Schematic diagram of the experimental apparatus.

cm^{-1}. Anal. Calcd for $C_{37}H_{45}N_3O_4$: C, 74.59; H, 7.61; N, 7.05. Found: C, 74.77; H, 7.42; N, 7.00.

2-(4′-(Perfluorobutyl)sulfonylphenyl)-6,9-bis(2′-ethylhexyloxy)-1H-phenanthro[9,10-d]imidazole (4f). A mixture of 1.0 g (2.15 mmol) of 3,6-bis(2-ethylhexyloxy)-9,10-phenanthrenedione (**16**), 0.88 g (2.26 mmol) of *p*-(perfluorobutyl)sulfonyl benzaldehyde, and 3.3 g (43 mmol) of ammonium acetate in 35 mL of acetic acid was heated to reflux for 3 h. The mixture was poured into ice water to give a yellow solid. The crude product was filtered through a pad of Celite, washed and dried. Purification by column chromatography on silica gel with 10% ethyl acetate in hexanes gave two fluorescent yellow products:

The lower R_f product was recrystallized from ethanol to give 1.0 g (58% yield) of the substituted phenanthro[9,10-*d*]imidazole **4f**: mp 111–113 °C; ^{1}H NMR δ (acetone-d_6) 8.59 (d, *J* = 8.8 Hz, 2H), 8.40 (d, *J* = 8.6 Hz, 2H), 8.19 (d, *J* = 8.7 Hz, 2H), 8.16 (d, *J* = 2.3 Hz, 2H), 7.33 (dd, *J* = 8.8 Hz, *J* = 2.3 Hz, 2H), 4.14 (d, *J* = 5.6 Hz, 4H), 1.84–1.77 (m, 2H), 1.66–1.49 (m, 8H), 1.45–1.36 (m, 8H), 0.99–0.80 (m, 12H): ^{13}C NMR δ (THF-d_8) 158.7, 146.1, 139.3, 132.5, 131.0 (br), 127.2, 124.2 (br), 117.0, 108.3 (br), 71.1, 40.7, 31.6, 30.1, 24.8, 23.9, 14.4, 11.5; IR (KBr) 3412, 2961, 2931, 2877, 2862, 1624, 1598, 1510, 1466, 1442, 1415, 1368, 1352, 1237, 1185, 1169, 1142, 1122, 1063, 1028, 842, 583 cm^{-1}. Anal. Calcd for $C_{41}H_{45}F_9N_2O_4S$: C, 59.13; H, 5.44; F, 20.53; N, 3.36; S, 3.85. Found: C, 59.05; H, 5.58; F, 20.78; N, 3.30; S, 3.81.

The higher R_f product, identified as 2-(4′-(perfluorobutyl)-sulfonyl)-6,9-bis(2′-ethylhexyloxy)-1*H*-phenanthro[9,10-*d*]oxazole **17**, was recrystallized from ethanol to give 0.36 g (20% yield) of yellow crystals: mp 148–151 °C; ^{1}H NMR δ (CDCl$_3$) 8.47–8.42 (m, 3H), 8.16 (d, *J* = 8.8 Hz, 1H), 8.10 (d, *J* = 8.5 Hz, 2H), 7.99 (d, *J* = 2.2 Hz, 1H), 7.97 (d, *J* = 2.2 Hz, 1H), 7.40–7.33 (m, 2H), 4.11 (d, *J* = 5.5 Hz, 2H), 4.10 (d, *J* = 5.5 Hz, 2H), 1.90–1.86 (m, 2H), 1.70–1.52 (m, 8H), 1.44–1.39 (m, 8H), 1.07–0.84 (m, 12H); ^{13}C NMR δ (THF-d_8) 159.8, 159.3, 145.8, 135.9, 135.1, 133.5, 132.7, 132.2, 131.2, 128.4, 124.8, 123.2, 121.1, 118.0, 117.8, 115.9, 115.2, 108.3, 108.2, 71.2, 40.7, 31.6, 30.1, 24.8, 23.9, 14.4, 11.5; IR (KBr) 2962, 2932, 2877, 2862, 1602, 1514, 1456, 1440, 1372, 1352, 1237, 1203, 1187, 1171, 1142, 1122, 1045, 840, 687, 584 cm^{-1}. Anal. Calcd for $C_{41}H_{44}F_9NO_5S$: C, 59.06; H, 5.32; F, 20.50; N, 1.68; S, 3.84. Found: C, 59.12; H, 5.53; F, 20.50; N, 1.62; S, 3.68.

Melting points (°C) for the remaining compounds were as follows: **1b**, 257; **1c**, 215; **1d**, 185; **1f**, 50–68; **1g**, 142; **1h**, 155; **1i**, 169; **1k**, 159; **2b**, 189; **2c**, 175; **2j**, 106; **2k**, 129; **2l**, 196; **2m**, 210; **2n**, 196; **4a**, 375; **4k**, 331. Thiazole **3e** is an oil at room temperature.

Characterization. Molecular hyperpolarizabilities were determined by electric-field-induced second harmonic (EFISH) experiments[38,39] as described previously.[12] The experimental apparatus is shown in Figure 2. The output of a Spectra-Physics GCR-3 laser was directed either along the optical table to the EFISH cell or diverted into a Raman shifter so that the backscattered Stokes radiation would be directed toward the cell. Thus, experiments could be performed at either 1064 or 1907 nm. For each wavelength, specific half-wave plates and notch filters for the photomultiplier tubes were required. A reference signal, proportional to the square of the laser intensity, was generated by focusing a part of the beam on a quartz wedge and detecting the resulting frequency-doubled light. The pulse energy of the light reaching the cell was controlled by the combination of the half-wave plate and a vertical polarizer. The beam quality was improved by a spatial filter. The spatial filter was necessary only for the Raman-shifted beam, but it was used for all experiments.

Pulse synchronization was achieved by slaving the laser, boxcar triggers, and high-voltage pulser to a Stanford Research Systems DG535 digital pulse generator. The DG535 (together with the motorized stage and the high-voltage power supplies for the photomultipliers) was controlled over the IEEE-488 bus by an IBM PS/2 model 80-071 computer. Adjustment of a single instrument was therefore sufficient to ensure that (i) the laser pulse coincided with the maximum of the high-voltage pulse, (ii) the boxcar gate coincided with the maximum signal out of the photomultipliers, (iii) the YAG laser pulse energy was optimized (accomplished by varying the Q-switch delay), and (iv) the high-voltage pulse was not being applied to the cell between scans while solutions were being changed (accomplished by dropping the amplitude of the trigger pulse for the high-voltage pulser at the conclusion of each scan).

For each solution, the cell was scanned perpendicular to the laser beam so that the path length changed continuously. The resulting oscillatory second harmonic signals were recorded and then fit to a sin^2 function to yield the signal amplitude (derived from the height of the peaks) and the coherence length (calculated from the spacing between the peaks). The solutions were referenced to a quartz standard each day, using standard values[5,40] for d_{11} of quartz (1.20×10^{-9} esu at 1064 nm and 1.04×10^{-9} esu at 1907 nm). For each chromophore, several solutions of varying concentration were prepared, and the frequency doubling of the laser was measured as a function of concentration. The concentration dependence was extrapolated to zero and combined

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(38) Bethea, C. G.; Levine, B. F. *J. Chem. Phys.* **1975**, *63*, 2666.
(39) Bethea, C. G. *Appl. Opt.* **1975**, *14*, 1447.
(40) Oudar, J. L. *J. Chem. Phys.* **1977**, *67*, 446.

with the concentration dependence of the solution dielectric constant to yield an experimental third-order susceptibility Γ, using the method of Singer and Garito.[41] In our calculations, the concentration dependence of n^2 and specific volume were assumed to be negligible; in general, they contribute only a few percent to Γ. The susceptibility Γ is equal to the sum of second- and third-order contributions.[40] In this work we assume that the third-order contribution is negligible; our measured hyperpolarizabilities thus represent upper limits.

The concentration dependence of the solution dielectric constant was used as an approximation for the quantity

$$\frac{(\epsilon - n^2) - (\epsilon_0 - n_0^2)}{C} \tag{1}$$

using again the assumption that the concentration dependence of n^2 is small. The Guggenheim expression[42] for the dipole moment can thus be rewritten as

$$\mu = \sqrt{\frac{27kT}{4\pi N_0(\epsilon_0 + 2)(n_0^2 + 2)} \frac{\partial\epsilon}{\partial C}} \tag{2}$$

Dielectric constants of solutions at 1 MHz were determined using a home-built solution capacitance cell and a Hewlett-Packard Model 4284A LCR meter. UV/vis spectra were recorded with a Hewlett-Packard Model 8452A diode array spectrophotometer; measured wavelengths were therefore good to ±2 nm. Values of $\lambda_{\max}$ measured from the absorption spectra were used to extrapolate β to zero frequency (β_0) according to the two-level model:[40,43]

$$\beta_0 = \beta_\omega\left(1 - \frac{\lambda_{\max}^2}{\lambda^2}\right)\left(1 - 4\frac{\lambda_{\max}^2}{\lambda^2}\right) \tag{3}$$

In this expression, β_ω is the quadratic molecular hyperpolarizability at frequency ω (corresponding to the laser source at wavelength λ), and β_0 is the two-level frequency-adjusted quadratic molecular hyperpolarizability.

For 1907-nm experiments, only chloroform was used as a solvent. FTIR spectra reveal that dioxane has overtone combination absorptions in this region, which cause the effective laser pulse energy at the fundamental wavelength to be less than the value implied by the quartz reference signal. More than 20% of the 1907-nm light is absorbed in a 1-mm path length. Therefore, all published hyperpolarizabilities measured in dioxane at 1907 nm should be regarded as lower limits unless solvent absorbance has been explicitly taken into account. The same holds true for tetrahydrofuran, whose overtone spectrum is similar to that of dioxane.

Results

The nonlinear optical chromophores prepared for this study are shown by structures **1–4** in Figure 1. In all cases the 2,4,5-triarylimidazoles **1a–i**, 2,4,5-triaryloxazoles **2a–c,j–n**, and the 2,4,5-triarylthiazoles **3a,e** are substituted with an electron-withdrawing group (A) at the para position of the 2-aryl ring and an electron-donating group (D) at the para positions of both 4-aryl and 5-aryl rings. Likewise, the phenanthro[9,10-*d*]imidazoles **4a,e,f,k** have an electron withdrawing group (A) at the para position of the 2-aryl ring and an electron donating group (D) at the 6 and 9 positions. The related series of compounds with the opposite donor–acceptor relationship, i.e., donor on the 2-aryl ring and acceptors on the 4-aryl and 5-aryl rings is currently under investigation. That class is less synthetically accessible, however, and molecular orbital calculations indicate that the compounds should possess smaller hyperpolarizabilities.

Table I. Nonlinear Optical Data for Substituted Triphenylimidzazoles[a]

compound	solvent	μ	$\lambda_{\max}$	$\lambda_{\exp}$	β	β_0	Q
1i	$CHCl_3$	8.3	476	1907	78.7	55.4	96.9
1g	dioxane	8.0	344	1064	53.2	27.7	64.4
1d	$CHCl_3$	7.2	438	1907	45.5	34.0	56.0
1b	dioxane	8.1	400	1064	69.1	25.8	52.2
1h	dioxane	6.6	398	1064	55.9	21.2	35.4
1a	dioxane	7.0	410	1064	52.3	18.1	30.9
1e	$CHCl_3$	6.3	416	1907	24.5	18.9	28.7
1a	$CHCl_3$	6.4	412	1907	19.9	15.4	23.9
1f	$CHCl_3$	6.5	384	1907	13.9	11.2	19.0
1c	dioxane	8.0	362	1064	10.1	4.8	10.6

[a] Donors and acceptors are shown in Figure 1. $\lambda_{\exp}$ refers to the wavelength at which the EFISH experiments were performed. Wavelengths are given in nm, hyperpolarizabilities in 10^{-30} esu, and dipole moments in debye. Q is defined in the text.

Table II. Nonlinear Optical Properties of Substituted Triphenyloxazoles[a]

compound	solvent	μ	$\lambda_{\max}$	$\lambda_{\exp}$	β	β_0	Q
2b	dioxane	7.1	378	1064	63.9	27.6	51.8
2n	$CHCl_3$	8.0	370	1064	31.5	14.3	30.8
2a	dioxane	6.3	390	1064	47.3	18.9	30.5
2k	dioxane	7.9	378	1064	31.1	13.4	28.0
2c	dioxane	7.0	358	1064	17.1	8.3	16.2
2m	dioxane	7.0	352	1064	15.6	7.8	15.5
2j	dioxane	5.7	344	1064	13.7	7.2	11.9
2l	dioxane	5.3	338	1064	9.2	4.2	7.7

[a] Donors and acceptors are shown in Figure 1. $\lambda_{\exp}$ refers to the wavelength at which the EFISH experiments were performed. Wavelengths are given in nm, hyperpolarizabilities in 10^{-30} esu, and dipole moments in debye. Q is defined in the text.

The nonlinear optical properties of the 2,4,5-triarylimidazoles **1a–i** are collected in Table I and the data for the 2,4,5-triaryloxazole derivatives **2a–e,j–n** appear in Table II.

Values of an arbitrary figure of merit Q were calculated for each compound. $Q = 100\mu\beta_0/\lambda_{\max}$, where μ is the ground state molecular dipole moment (in debye) which determines the alignment upon poling, β_0 is expressed in units of 10^{-30} esu, and $\lambda_{\max}$ is the long-wavelength absorption maximum (in nanometers) and is an indication of the molecular transparency. For frequency-doubling applications, transparency is vital; a figure of merit for that specific application would probably include $\lambda_{\max}^2$ in the denominator, to cancel out the quadratic dependence on $\lambda_{\max}$ of β_0 according to the two-level model.[43] For electrooptical applications, transparency is less important, so a specific figure of merit would probably not include $\lambda_{\max}$. To make Q more general, we include the maximum absorbance wavelength to the first power in the denominator. Since $\mu\beta$ is the quantity measured by EFISH, the uncertainty in Q is smaller than the uncertainty in β because the error in the dipole moment determination is not included. Compounds in Tables I and II are therefore listed in order of descending Q value.

There are a number of examples in Tables I and II where the substitution patterns are the same for both the imidazoles and the oxazoles, and these data are collected in Table III for direct comparison. Also included in this table are the related data for the thiazole **3a** to allow comparison with imidazole **1a** and oxazole **2a**, each with a 2-(nitrophenyl) acceptor and 4,5-(4′-methoxyphenyl) donors.

The molecular geometries of these three identically substituted triarylimidazoles, oxazoles and thiazoles, **1a–3a**, were also probed computationally. Initial geometries

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(41) Singer, K. D.; Garito, A. F. *J. Chem. Phys.* **1981**, *75*, 3572.
(42) Guggenheim, E. A. *Trans. Faraday Soc.* **1949**, *45*, 714.
(43) Oudar, J. L.; Chemla, D. S. *J. Chem. Phys.* **1977**, *66*, 2664.

Table III. Comparison of Imidazole, Oxazole, and Thiazole Data[a]

compound	μ	λ_{max}	β_0	Q
imidazole **1a**	7.0	410	18.1	30.9
oxazole **2a**	6.3	390	18.9	30.5
thiazole **3a**	8.1	400	21.1	42.7
imidazole **1b**	8.1	400	25.8	52.2
oxazole **2b**	7.1	378	27.6	51.8
imidazole **1c**	8.0	362	4.8	10.6
oxazole **2c**	7.0	358	8.3	16.2

[a] Data taken from Tables I and II. Each set of data for a given donor/acceptor pair was acquired in the same solvent and at the same wavelength.

were obtained by MMX molecular mechanics techniques contained within the ALCHEMY molecular graphics package, and these data were subjected to further minimization using the semiempirical PM3 procedure[44,45] within the commercially available MOPAC package.

Geometry minimization calculations on the group of nitro/methoxy substituted imidazole **1a**, oxazole **2a**, and thiazole **3a** molecules suggested significant steric interactions between the substituents in the heterocyclic ring positions 4 and 5. This steric interaction was manifested by twisting of the adjacent donor substituted 4,5-aromatic substituents around the single bonds joining them to the parent heterocycle causing a loss in coplanarity between the donor substituents and the azole ring. As expected, this distortion from coplanarity was most severe for aromatic substituents in the 4,5-positions and is less apparent for the aromatic substituent located in position 2. For derivatives with a 2-(4′-nitrophenyl) group, the steric interaction of the electron deficient aromatic moiety with the adjacent heteroatoms of the azole system is apparently minimal, and the *p*-nitrophenyl substituent remains almost coplanar (torsional angles <10°) with the azole ring. The extent of twisting of the 4,5-substituents depends both on the position of attachment and the nature of the heterocyclic ring. PM3 geometry minimization calculations suggest that the overall distortion from coplanarity is smallest for the oxazole derivative and largest in the case of the thiazole. For compounds with 4,5-bis-(4′-methoxyphenyl) groups, the calculated distortions from coplanarity with the heterocyclic ring for the phenyl ring in position 4 are 29°, 15°, and 45° for the imidazole, oxazole, and thiazole, respectively. The related values for the phenyl ring in position 5 are 69°, 37°, and 83°, respectively.

The X-ray crystal structure[46] of 2-(4′-nitrophenyl)-4,5-bis(4′-methoxyphenyl)imidazole **1a** is consistent with the theoretical predictions. In the solid state, the *p*-nitrophenyl substituent is nearly coplanar with the heterocyclic imidazole ring (angle ~15°), while the donor substituted aryl rings are strongly twisted, forming dihedral angles of 26.5 and 47.7°, respectively. Inspection of molecular models suggests that this distortion is caused, to a large extent, by the unfavorable "peri"-type steric interactions between the geometrically proximate ring hydrogens (α to the heterocyclic connection) of the aromatic donor substituents. Loss of coplanarity between the donor and acceptor groups interacting electronically through the heterocyclic ring would be expected to affect the linear spectroscopic properties and to decrease the quadratic molecular hyperpolarizabilities (see below).

Table IV. Comparison of Planar and Nonplanar Triphenylimidazoles[a]

compound	μ	λ_{max}	β_0	Q
1e (nonplanar)	6.3	416	18.9	28.7
4e (planar)	5.5	436	25.5	32.2
1f (nonplanar)	6.5	384	11.2	19.0
4f (planar)	5.9	416	23.6	33.4

[a] All compounds measured in chloroform solution at 1.907 μm.

Relief of the unfavorable aromatic ring hydrogen interactions is achieved by directly bonding the alpha carbon atoms of the two 4,5-aromatic substituents to produce a planar polycyclic phenanthrene unit as shown in structure 4. Such an arrangement ensures virtual coplanarity between the electron-donor substituents, the heterocyclic ring and the electron-acceptor group, assuming the latter is not significantly twisted.

The 2-phenyl-6,9-dialkoxyphenanthro[9,10-*d*]imidazoles **4a,e,f,k** are thermally stable, high melting materials. When the donor groups are methoxy, as in **4a** and **4k**, the products are very high melting (>300 °C) and are insoluble in most common organic solvents. The incorporation of longer branched chain alkyl substituents, e.g., 2-ethylhexyl groups as in **4e** and **4f** leads to lower melting materials with excellent solubilities. Only the latter two materials were soluble enough to permit EFISH evaluation. The nonlinear optical properties of the planarized derivatives **4e,f** were determined, and the data appear in Table IV together with those of the model nonplanar imidazoles. More detailed linear optical data for the planarized materials **4e,f,k** are collected in Table V together with those of comparably substituted, but nonplanar, imidazoles. Among the latter is imidazole **1k**, which was also insufficiently soluble in common solvents for EFISH measurements.

Discussion

The triarylazoles show excellent thermal stability and solubility in common organic solvents, have sufficient dipole moments for effective poling, and possess substantial microscopic nonlinearity. One of the main virtues of these compounds is their surprising miscibility with polymers. Most of these materials are soluble in a variety of common polymers, including high-temperature thermoplastics such as polyimides, polyquinoxalines, and poly(ether sulfones). For example, in some cases as much as 50% by weight mixtures of these chromophores can be prepared in commercially available polyimides without phase separation.[23]

Most of the substituted triarylazole derivatives in this study were high-melting, thermally stable materials. For example, thermogravimetric analysis (TGA) of **1a**, **2a**, and **3a** (selected to probe any influence of the different heterocyclic rings) showed only a few percent weight loss at 300 °C followed by a catastrophic weight loss with onset in the range 320–350 °C. In this region, differential scanning calorimetry (DSC) analysis also indicated the onset of an exothermic reaction signifying the decomposition of the chromophore. Although there are slight differences in the thermal behavior of **1a**, **2a**, and **3a** under the conditions of analysis, the thermal stabilities of the three heterocyclic compounds appear comparable. The feature which limits the stability seems to be the exact nature of the donor and acceptor combination. For the specific combination of alkoxy donors and nitro acceptors,

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(44) Stewart, J. J. *Comput.-Aided Mol. Des.* **1990**, *4*, 1.

(45) Stewart, J. J. *Comput. Chem.* **1989**, *10*, 209.

(46) Inouye, Y.; Sakaino, Y. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 3295.

as in **1a**, **2a**, and **3a**, we have never observed decomposition onset temperatures in excess of the range 300–350 °C. The exact nature of the alkoxy substituent seems relatively unimportant, with little difference in thermal stability observed for methoxy and 2-ethylhexyloxy substitution in those examples which also contain a nitrophenyl acceptor group. Preliminary studies suggest, however, that aryl ether donors provide enhanced stability relative to simple alkoxy substituents in combination with nitro acceptor groups. Materials with dialkylamino donor substituents, as in **1d** and **1i**, in combination with nitro acceptors begin to show weight losses by TGA and an exothermic decomposition by DSC at temperatures 50–75 °C lower than the corresponding derivatives with alkoxy donors. The mechanism of degradation of the nitro-containing chromophores is probably thermooxidative in nature, since nitrobenzene itself is a well-known reagent for oxidation of a wide range of functional groups, especially at elevated temperatures.

The thermal stability of **1a** dispersed in a polyimide host has also been investigated. The host was a 50–50 copolymer of oxydiphthalic anhydride and the diamines 4,4′-oxydianiline and 9,9-bis(*p*-aminophenyl)fluorene. Spectra of samples of a 15 wt % mixture of **1a** in the polyimide were taken before and after each sample was held for an hour at a particular temperature, and decomposition loss was detected by shifts and decreases in the absorption bands. At 250 °C, there was no detectable loss. At 300 °C, loss was less than 5%. (At that temperature, samples with Disperse Red 1 chromophore showed enormous loss.) At 350 °C, the lophine underwent substantial decomposition in an hour. These results were completely consistent with the DSC and TGA data, indicating that the latter are good indicators of the level of thermal stability in these chromophores.

The thermal stabilities of chromophores substituted with alkylsulfonyl or perfluoroalkylsulfonyl acceptor groups are usually comparable to, or slightly better than, the nitro-substituted materials. Phenylsulfonyl substitution, however, often leads to materials with even better thermal stability. The parent unsubstituted triarylimidazole ring systems themselves have excellent thermal stability and have found some use in the preparation of high-temperature thermoplastics. For example, an aromatic polyether containing a 2-phenyl-4,5-bis(aryloxy)-imidazole group can be routinely processed in air at 300 °C and suffers less than 5% weight loss under nitrogen at temperatures up to 500 °C.[47]

All of the chromophores have substantial ground-state dipole moments (essential for electric field poling applications) and possess significant microscopic optical nonlinearities. Surprisingly, the dipole moments of the planar derivatives are always lower than those of the comparably substituted nonplanar derivatives. The nonlinearity depends primarily on the particular combination of D–A substituents and to a lesser extent on the nature of the heterocyclic ring present.

A number of conclusions may be drawn based on imidazole data shown in Table I. Amino donors result in both a red-shift in the absorption spectra and a significant increase in the intrinsic molecular hyperpolarizability relative to comparable alkoxy and arylthio donor compounds. Unexpectedly, chromophore **1i**, containing cyclic hexamethyleneimine (homopiperidine) donors, both absorbs at longer wavelengths and is significantly more nonlinear than chromophore **1d**, which contains piperidine substituents. The substantial enhancement of the nonlinearity upon addition of two methylene units to the donor rings is still a mystery under investigation at this point. Extension of the conjugation length of the donor by addition of a phenylacetylene linkage as in chromophore **1g** also increases the nonlinearity relative to **1a** and produces a significant red shift in the absorption spectrum ($\Delta\tilde{\nu} = 1559\ \text{cm}^{-1}$). In the case of **1b**, where the acceptor is extended, there is a slight blue shift in the chromophore ($\Delta\tilde{\nu} = 610\ \text{cm}^{-1}$) and the hyperpolarizability is reduced. Replacement of the nitro acceptor group by a phenylsulfonyl substituent, as in chromophore **1c**, results in a large drop in the nonlinearity and is also accompanied by a significant blue-shift in the absorption spectrum ($\Delta\tilde{\nu} = 3234\ \text{cm}^{-1}$).

Compound **1a** was characterized at both 1064 and 1907 nm. The results give an estimate of the accuracy of β_0 extrapolations when the absorbance maximum (λ_{max}) is used to approximate the energy difference between ground and excited states. One would predict that the correct effective wavelength to use in such extrapolations (λ_{eff}) would lie between the absorbance maximum and the 0–0 band ($\lambda_{0\text{–}0}$). Normally, one measures one value of β_ω and uses λ_{max} and eq 3 to determine β_0. With data at two wavelengths, one can determine both β_0 and λ_{eff} from the data. For compound **1a**, β_0 was 14.8×10^{-30} esu and λ_{eff} was 439 nm, if we use the dipole moment value that was measured in chloroform. A separate fluorescence experiment on this compound showed that the 0–0 band (overlap between absorption and emission fluorescence spectra) was approximately 488 nm. Since λ_{max} (412 nm) is closer to the effective excitation wavelength (439 nm) than is $\lambda_{0\text{–}0}$ (488 nm), λ_{max} is the better wavelength to use in two-level model determinations of β_0 if EFISH data are available at only one wavelength. Nevertheless, more accurate values of β_0 are obtained by taking EFISH data at two wavelengths, because the true excitation wavelength is a result of the calculations rather than an approximated input.

The effect of the acceptor substituent on the oxazoles (Table II) was similar to that observed for the imidazoles. Nitro substitution, as is found in chromophore **2a**, again results in large nonlinearities and red-shifted absorptions. Extension of the acceptor conjugation length via a phenylacetylene linkage, as in chromophore **2b**, results in both an increased nonlinearity and a blue-shifted absorption maximum ($\Delta\nu = 814\ \text{cm}^{-1}$). Although sulfone acceptor groups such as in chromophores **2c** and **2m** result in much lower nonlinearities relative to nitro substitution, some of this loss can be recovered by fluorination, as in the case of perfluoroalkyl sulfone **2k** or perfluoroalkyl-substituted aryl sulfone **2n**. Even simple perfluoroalkyl substitution, as found in compounds **2j** and **2l**, provides materials with significant nonlinearities, while further blue-shifting the long wavelength absorption maxima. Chromophore **2n** contains an acceptor group which is a composite of both phenyl sulfone and perfluoroalkyl acceptors. The nonlinearity of this compound is also correspondingly larger while the thermal stability is still excellent (decomposition onset at 432 °C).

The imidazole–oxazole comparisons (Table III) show consistent trends. The oxazole dipole moments are

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[47] Connell, J. W.; Hergenrother, P. M. *J. Polym. Sci., Part A. Polym. Chem.* **1991**, *29*, 1667.

Table V. Comparison of Spectral Properties of Planar and Nonplanar Azoles[a]

compound	mp	λ_{max}	ϵ_{max}	$\Delta\bar{\nu}$	f
		Planar			
4e	171	432	25 100	4630	0.47
4f	121	412	35 000	3880	0.54
4k	320	410	32 800	3930	0.52
		Nonplanar			
1a	222	410	21 100	5190	0.43
2a	212	392	17 600	5750	0.40
3a	150	400	15 000	5090	0.31
1f	160	387	23 900	4470	0.43

[a] All spectra taken in dioxane solution. Melting points expressed in degrees Celsius; λ_{max} in nm; molar extinction coefficients ϵ_{max} in M^{-1} cm^{-1}; and absorption peak full widths at half-maximum $\Delta\bar{\nu}$ in cm^{-1}. f is the calculated oscillator strength.

uniformly smaller by a full debye; the oxazole absorptions are blue-shifted; and the oxazole hyperpolarizabilities are greater. The net result is that the Q factors for imidazoles and oxazoles tend to be the same within experimental error. A reasonable explanation for this result is that the dipole moments of the excited states for the two heterocycles are similar, so that the difference in dipole moments between ground and excited states is larger for the oxazoles. The intrinsic hyperpolarizability β_0 is proportional to that difference,[45,47] as well as to $(\lambda_{max})^3$ and the oscillator strength. Since the oscillator strengths of the oxazoles do not appear to be noticeably larger than those of the imidazoles, and the absorption maxima are demonstrably bluer, $\Delta\mu$ for the oxazoles must be higher than for the imidazoles. This hypothesis is currently being studied by fluorescence solvatochromism. The net result is that the oxazoles have greater nonlinear response but are more difficult to orient in order to take advantage of that response.

The thiazole derivative has both a larger ground-state dipole moment and improved nonlinearity (relative to the comparably substituted imidazole and oxazole) and absorbs in the same region. This combination of features results in a larger value of Q for the thiazole. On the basis of this single series, we conclude that the intrinsic nonlinearities of triaryl substituted azole derivatives increase in the order imidazoles < oxazoles < thiazoles, although the differences are not very large.

The β_0 values for the planar derivatives were larger than those of the nonplanar compounds, as anticipated (Table IV). The β_0 value for the nitro derivative **4e** is also greater than that of the fluorinated sulfone **4f**, consistent with the relative electron-attracting nature of the respective substituents. Therefore, it is remarkable that the measured hyperpolarizability of the planarized perfluoroalkyl sulfone **4f** is substantially larger than that of the nonplanar nitro-substituted triarylimidazole **1a**. The analogous amino-substituted planarized phenanthroimidazole analogues should possess even larger nonlinearities relative to the alkoxy-substituted phenanthro[9,10]imidazoles examined thus far.

The spectroscopic properties of the planarized derivatives (Table V) are interesting in a number of ways. First, the absorption maxima are red-shifted compared to the comparable triarylimidazoles (compare **4e** with **1e** and **4f** with **1f**, as in Table IV). This was anticipated, since the donor substituted benzene rings in **1a** and **1b** must be twisted to relieve steric congestion, thus affecting the conjugation of the π-systems. Just as striking, however, is the significant increase in the molar extinction coefficients at λ_{max} for the planarized derivatives. The spectral bandwidths of the long wavelength absorption bands of fluorinated sulfones **4f,k**, as measured by the full widths at half-maximum (fwhm), are considerably less than for the nitro derivative **4e**. Likewise, the fwhm's of the long wavelength transitions are smaller for the more rigid planar derivatives than for the nonplanar materials, but the concomitant increase in the molar extinction coefficients of the planar derivatives suggests that the oscillator strengths of the former will be larger. The data in Table V show that this is indeed the case. The number calculated for the nitro derivative **4e** is probably a lower limit, since recent measurements on other soluble derivatives have yielded values ranging from 0.47 to 0.52. Because the oscillator strength of an electronic transition and the molecular hyperpolarizability are both proportional to (μ_i^2), the square of the transition dipole moment,[48] it is reasonable that the planarized imidazoles should be more nonlinear than comparably substituted, but nonplanar, triarylimidazoles. This, in conjunction with the red-shifted absorption maxima of the planar derivatives, probably accounts for the increased molecular hyperpolarizabilities of the planar derivatives.

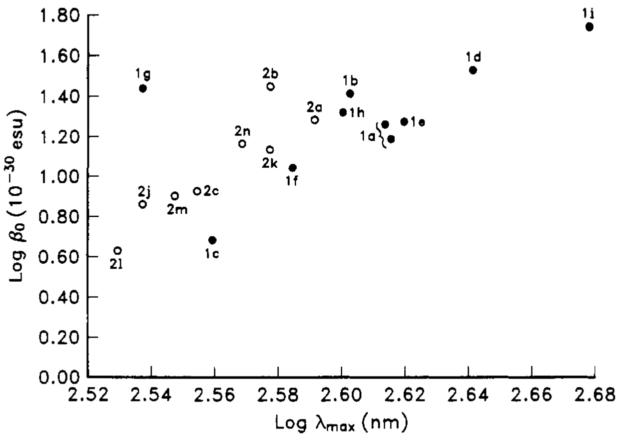

Figure 3. Nonlinearity–transparency plot for triphenylimidazoles and triphenyloxazoles.

It has become traditional to quantify the empirical tradeoff between nonlinearity and transparency for a given class of compounds by fitting a straight line to a plot of log β vs log λ_{max} and determining the slope of the best-fit line.[49] Figure 3 shows logarithmic plots (using β_0) for the imidazoles and oxazoles, respectively. For the imidazoles, the scatter is large for the low λ_{max} points. If the two compounds with greatest deviation, **1g** and **1c** (one above and one below the others), are not included, the slope is 6.5 ± 1.4. For the oxazoles, the slope is 11.0 ± 2.0. Therefore, a structural modification of a triaryloxazole that leads to a red-shift in the long wavelength absorption tends to induce a greater increase in the quadratic hyperpolarizability than does the equivalent modification on a triarylimidazole. The intercepts are −15.7 ± 3.8 for the imidazoles and −27.2 ± 5.2 for the oxazoles. The difference in least-squares parameters corresponds to substantial differences in predicted β_0 values; an oxazole with a λ_{max} of 400 nm would have a predicted β_0 of 26.5 × 10^{-30}, whereas the corresponding imidazole value would

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(48) Turro, N. J. In *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978; Chapter 5.

(49) Cheng, L. T.; Tam, W.; Feiring, A.; Rikken, G. *Proc. SPIE—Int. Soc. Opt. Eng.* **1990**, *1337*, 203.

be 16.3×10^{-30}. Recall, though, that for identical substituents, the imidazole has a longer λ_{max}; this reduces the differences between the predicted hyperpolarizabilities.

Conclusions

A variety of substituted triphenylimidazoles, -oxazoles, and -thiazoles have been prepared and characterized. These materials show exceptional thermal stabilities, have respectable dipole moments, and are significantly nonlinear. This combination of properties suggests potential utility for these materials when incorporated into high temperature polymers, either as host–guest arrays or when tethered or incorporated into the polymer backbone. The chromophore nonlinearity depends primarily on the type of substituents and secondarily on the nature of the conjugating heterocyclic ring. Considering only the intrinsic quadratic molecular hyperpolarizabilities, available data indicate that for comparable substitution and geometries, the order of nonlinearity is imidazoles < oxazoles < thiazoles, although these differences are not large. When transparency issues are important, it appears that the oxazoles are also slightly superior to the imidazoles. Planarization of the 4,5-donor rings by the formation of a polycyclic phenanthrene aromatic core results in a significant increase in the oscillator strength of the long-wavelength transition and also in the quadratic molecular hyperpolarizability without adversely affecting the thermal stability of the chromophore. Initial data also suggest that the nonlinearity vs transparency tradeoff is also superior for the planarized phenanthroimidazoles vs their nonplanar triarylimidazole counterparts. Triaryl-substituted azole nonlinear optical chromophores represent progress toward the criteria which must be met before application of organic materials in practical nonlinear optical devices[50] becomes a reality.

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(50) Williams, D. J., In *Electronic and Photonic Applications of Polymers*; Bowden, M. J., Turner, S. R., Eds.; Advances in Chemistry 218; American Chemical Society: Washington, DC, 1989; pp 297–330.