are shown to be comparable.

It is possible to fully decompose the $BaCO_3$ in the 700–750 °C range by using vacuum processing with small initial particles. When this powder is then exposed to oxygen at ~750 °C, a majority of the 1-2-3 phase is obtained. Virtually complete conversion to the 1-2-3 phase is obtained at 800 °C.

Acknowledgment. We thank H. M. O'Bryan for helpful discussions.

Synthetic Approaches to Head-to-Tail Linked Azo Dyes for Nonlinear Optical Applications

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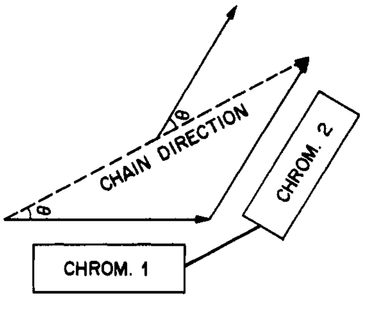
Two pathways for the synthesis of dipolar, main-chain azo dye oligomers were investigated. The first involves amide coupling of an *N*-arylpiperazine with a cyanocinnamic acid terminated azo dye, while the second depends upon Knoevenagel condensations of piperazinamides of cyanoacetic acid with (arylazo)benzaldehydes. The amide coupling was successful in the case of *N*-phenylpiperazine but failed with ((arylazo)phenyl)piperazines. The Knoevenagel condensation was more general and made possible the syntheses of a dimeric azo dye and an oligomeric azo dye mixture with the desired connectivity. The principal molecular moments of the chromophores in these oligomers, when in extended conformations, are significantly additive so that we might expect poled polymeric materials containing these oligomers to exhibit larger hyperpolarizabilities than would materials containing analogous, monomeric chromophores. Dipole moment measurements on the dimer and on models of its two "halves" confirmed this additivity.

Introduction

Second-order nonlinear optical materials consisting of azo dyes poled in polymer matrices have been considerably advanced[1] since the prototypical Disperse Red-1-poly(methyl methacrylate) (DR1–PMMA, 11-PMMA) system was first reported.[2] The use of cyanovinyl groups as electron acceptors, resulting in increased values of β and μ,[3] and corona poling, which increases the orienting electric field, has led to materials with electrooptic figures of merit comparable to those of lithium niobate.[1a,c] Furthermore, some of these materials have been shown to exhibit useful activity in devicelike structures.[4]

The first dye–polymer materials fabricated for nonlinear optics were two-component solutions.[2,5] Because of the molecular motion of the solute dyes, even in the glassy state, much of the orientation imparted to the dyes during poling is lost in a matter of days to weeks. The decay in orientation, and thus in the nonlinear optical properties, has been mitigated in more recent materials by covalent attachment of the chromophores to the polymer host, as well as by increasing the length of the chromophoric molecules.[1b]

The highest order parameter achieved so far with the azo dyes currently employed is about 20% so that relatively little of the cumulative second-order nonlinear susceptibility of the individual dye moieties is translated into the bulk hyperpolarizability. One means of increasing the poling-induced order while keeping the chromophores covalently bound to long, polymeric molecules would be to assemble the active species in a head-to-tail fashion so that their dipole moments would necessarily add, and each chromophore would be oriented by the electric field acting on the larger cumulative dipole moment. A detailed theoretical treatment of such an approach has recently appeared, along with initial experimental results.[6] For a chain of chromophores whose β and μ vectors are almost coincident with the vectors connecting the points of attachment of the respective monomer units to the chain, the degree of orientational enhancement possible is proportional to the average $n \cos^2 \theta$, where θ is the angle of those vectors with respect to the overall chain direction and n is the degree of polymerization. A polymer that is "stretched out" so that the dipolar chromophores point from the beginning of the chain to the end will display a large enhancement, while one in which the chromophores point in uncorrelated directions will show a negligible enhancement or even a diminution of effective dipole moment per chromophore.



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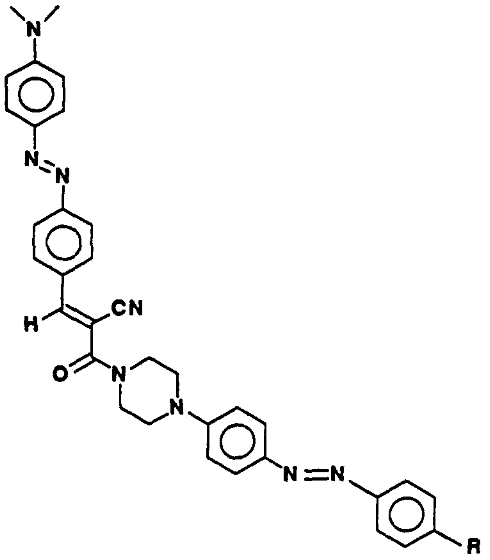
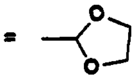
Tractable head-to-tail polymers that have been reported for nonlinear optical applications contain extremely flexible polymethylene chains as linking groups and employ donors weaker than the anilino group.[6,7] Thus, the chromophore vectors are not necessarily correlated, and the nonlinear susceptibilities of the chromophores are not as high as they might be. We have already devised synthetic methodology for the construction of oligomers of (cyanovinyl)anilines in which the average angle of connection between monomers is constrained to be 110° by virture of a piperazinyl spacer unit and amide linkage between chromophores.[8] In a stretched-out conformation, where the angle of each chromophore vector with respect to the overall chain direction would be about 35°, the enhancement would be 0.7n.

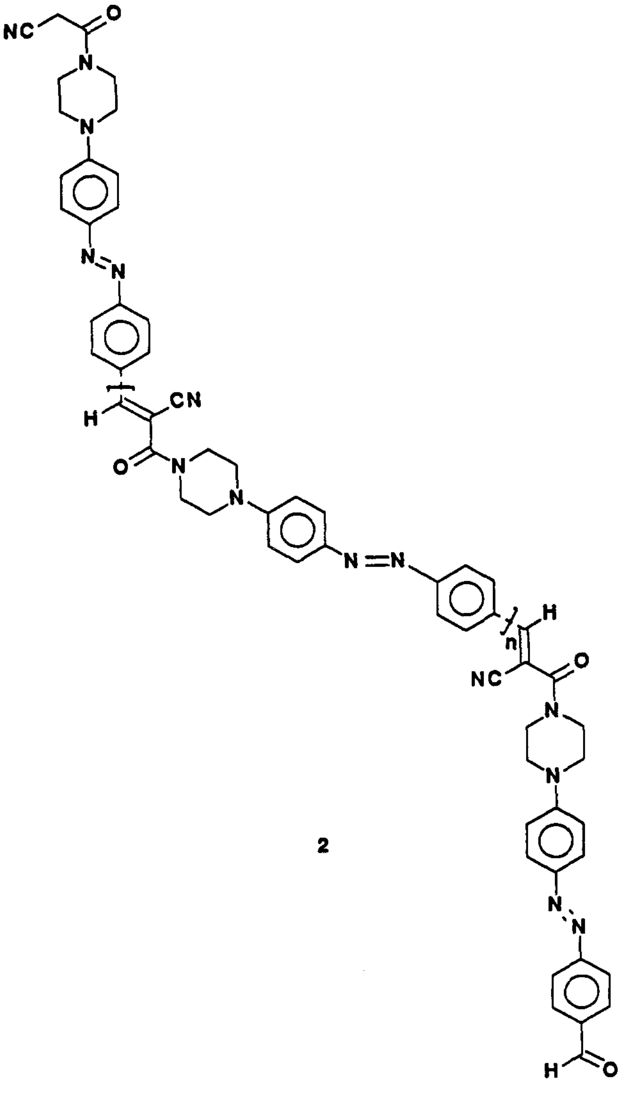


1 a. R = NO_2

b. R = CHO

c. R =





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In this manuscript, we extend this concept to the synthesis of oligomeric azo dyes, whose chromophores possess much higher β values than the simple cinnamoyl derivatives. Preliminary experiments indicated that the chemical behavior of amino- and carboxy-substituted cyanovinyl azo dyes is substantially different from that of the cyanocinnamates previously investigated. We therefore considered two different routes to the desired oligomers, culminating in the successful synthesis of a head-to-tail bis azo dye, **1a**, and a head-to-tail oligomeric dye mixture, **2**. The merits of the possible synthetic protocols, characterization of the products and intermediates, and pertinent observations on the individual reactions are discussed. Dipole moment measurements on **1a** and on models of its two "halves" confirm the expected segment-to-segment additivity of the molecular moments enforced by the piperazinamide linkage.

Experimental Section

General Procedures. NMR spectra, expressed as parts per million (ppm) relative to internal tetramethylsilane, were recorded on a Bruker AM 360 spectrometer. Mass spectral data were obtained on a Hewlett-Packard 5985B spectrometer. Molecular weights were obtained by gel permeation chromatography on a Beckman HPLC using a Waters Model 481 UV detector. GPC on the azo dyes was carried out on a 50-Å μ-Spherogel column, 7.5 mm i.d. × 30 cm long, using CH_2Cl_2 as the solvent with detection at 490 nm, unless otherwise specified. Retention volumes were determined at ambient temperature and 1 mL/min flow rate relative to compounds of known structure (e.g., **3** and **5**) run under identical conditions. Elemental analyses and the molecular weight determination were performed by Galbraith Laboratories. Dipole moments were measured as previously described.[8] Chloroform was distilled from P_2O_5 immediately before use.

2-Cyano-3-[([4-(*N*,*N*-dimethylamino)phenyl]azo)phenyl]propenoic Acid, 4. Cyanoacetic acid (0.85 g, 0.01 mol) and **5** (2.5 g, 0.01 mol) in EtOH (100 mL) were heated at reflux with piperidine (3 drops) for 2 h. H_2O was added to precipitate the product, which was isolated in 94% yield: mp 185 °C (dec): ^1H NMR (CD_3OD) δ 3.15 (s, 6 H, CH_3), 6.83 (d, 2 H, Ar), 7.88 (m, 4 H, Ar), 8.10 (d, 2 H, Ar), 8.20 (s, 1 H, =CH).

1-[2-Cyano-3-[([(*N*,*N*-dimethylamino)phenyl]azo)phenyl]propenoyl]-4-phenylpiperazine, 3. Method A. DCC (Aldrich, 0.062 g, 0.3 mmol) was added to a solution of **4** (0.1 g, 0.3 mmol) and *N*-phenylpiperazine (Aldrich, 0.049 g, 0.3 mmol), dissolved in CH_3CN at 0 °C, and the stirring continued for 2 h.

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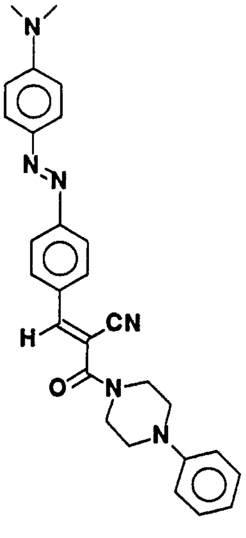

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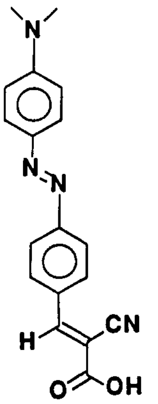

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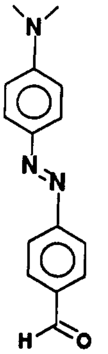

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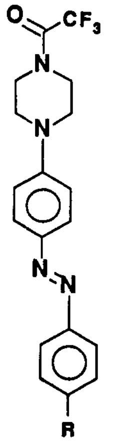
The solution was filtered, H_2O (10 mL) was added, and the CH_3CN was evaporated. CH_2Cl_2 was added to the aqueous solution, and the organic layer was separated, dried (Na_2SO_4), filtered, and evaporated. The product was isolated in 30% yield (0.050 g) by TLC on silica gel (2 mm, 50% ethyl acetate (EtOAc)/50% hexane).

Method B. Compounds **5** (0.56 g, 2 mmol) and **8b** (0.45 g, 2 mmol) were dissolved in EtOH, piperidine[15] (1 drop) was added, and the solution was heated at reflux overnight. The EtOH was evaporated and the product isolated by column chromatography on silica gel (EtOAc): yield, 0.7 g (71%); ^1H NMR ($CDCl_3$) δ 3.05 (s, 6 H, CH_3), 3.20 (m, 2 H, CH_2), 3.25 (m, 2 H, CH_2), 3.62 (m, 2 H, CH_2), 3.80 (m, 2 H, CH_2), 6.72 (d, 2 H, Ar), 6.93 (m, 3 H, Ar), 7.28 (m, 4 H, Ar), 7.50 (d, 2 H, Ar), (7.85 (m, 3 H, 1 H =CH, 2 H Ar); mass spectrum, *m/e* (rel intensity) 464 (5), 303 (8), 120 (100); GPC retention volume, 6.4 mL.

1-[(4-[4-(Trifluoroacetyl)piperazinyl]phenyl)azo]-4-nitrobenzene, 6a. A solution of 1-(trifluoroacetyl)-4-phenylpiperazine[8] (1 g, 4 mmol) and 4-nitrobenzenediazonium tetrafluoroborate (Aldrich, 0.92 g, 4 mmol) in HOAc was stirred for 30 min. Solid NaOAc (0.33 g, 4 mmol) was added over 10 min, and a precipitate began forming immediately. After stirring overnight, the solution was filtered and the collected solid was washed thorougly with H_2O and dried. The product was purified by column chromatography on silica gel (EtOAc) to yield 1.3 g (80%) of **6a**: ^1H NMR ($CDCl_3$) δ 3.50 (m, 4 H, CH_2), 3.84 (m, 2 H, CH_2), 3.90 (m, 2 H, CH_2), 6.98 (d, 2 H, Ar), 7.95 (m, 4 H, Ar), 8.35 (d, 2 H, Ar).



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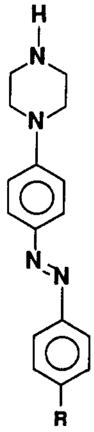

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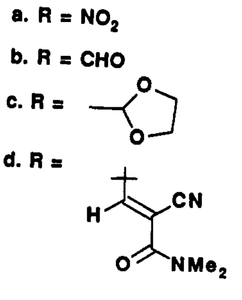

1-([(4-Piperazinyl)phenyl]azo)-4-nitrobenzene, 7a. Compound **6a** (0.1 g, 0.25 mmol) was dissolved in pyridine (2 mL) with heating and 1 mL each of MeOH and H_2O were added. Tetrabutylammonium hydroxide (Alfa, 0.25 g (55% solution), 0.5 mmol) was added, and the reaction mixture was stirred at 80 °C for 2 h. After evaporating the solvents, the residue was triturated with MeOH and dried. The piperazine nitrogen was deprotonated by refluxing the solid in alcoholic NaOH, extracting into toluene, washing with aqueous NaOH (pH 12), drying the organic layer, and evaporating: yield, 0.037 g (60%); ^1H NMR ($CDCl_3$) δ 3.05 (m, 4 H, CH_2), 3.40 (m, 4 H, CH_2), 6.98 (d, 2 H, Ar), 7.95 (m, 4 H, Ar), 8.35 (d, 2 H, Ar).

1-(2-Cyano-3-[([4-(-*N*,*N*-dimethylamino)phenyl]azo)phenyl]propenoyl)-4-(4-[(nitrophenyl)azo]phenyl)piperazine, 1a. Method A. Compound **3** (0.05 g, 1 mmol) and 4-nitrobenzenediazonium tetrafluoroborate were reacted, as described above for the preparation of **6a**, to give **1a** in 15% yield.

Method B. Compounds **5** (0.17 g, 0.7 mmol) and **9a** (0.25 g, 0.7 mmol) were "dissolved" in a minimum of NMP (5 mL). Piperidine (3 drops) was added and the solution heated at 80 °C for 3 h. The reaction was monitored by TLC (silica gel, EtOAc (50%)/hexane (50%)) until **5** was completely reacted. After cooling the reaction mixture to room temperature, CH_2Cl_2 (10 mL) and H_2O (5 mL) were added, and the organic layer was separated, dried (Na_2SO_4), evaporated, and dried overnight under vacuum to remove the residual NMP. The red solid was alternately triturated with CH_3CN, dissolved in CH_2Cl_2, and filtered to remove excess **9a**, three times. Compound **1a** was isolated by evaporating the final CH_2Cl_2 solution: yield, 0.16 g (37%); ^1H NMR ($CDCl_3$) δ 3.10 (s, 6 H, CH_3), 3.60 (m, 4 H, CH_2), 3.95 (m, 4 H, CH_2), 6.75 (d, 2 H, Ar), 6.98 (d, 2 H, Ar), 7.90 (m, 11 H, 1 H =CH, 10 H Ar), 8.32 (d, 2 H, Ar); GPC retention volume, 6.2 mL. Anal. Calcd for $C_{34}H_{31}N_9O_3$: C, 66.5; H, 5.1; N, 20.6. Found: C, 65.7; H, 5.2; N, 19.1. MW calcd 613.68, found 594 (vapor pressure osmometry, DMF).

1-[(4-[4-(Trifluoroacetyl)piperazinyl]phenyl)azo]-4-benzaldehyde, 6b. A solution of 4-aminobenzaldehyde (TCI American, 1.2 g, 0.011 mol) in H_2O (5 mL)/HCl (1 mL) was cooled to 0 °C, and ice (5 g) and HCl (1.5 mL) were added with stirring. Sodium nitrite (0.7 g, 0.01 mol) in H_2O (1.5 mL) was added dropwise to the acid solution over 15 min, maintaining the temperature below 5 °C, and the solution was stirred for an additional 15 min. A solution of 1-(trifluoroacetyl)-4-phenylpiperazine (2.6 g, 0.01 mol) in HOAc (10 mL) was added slowly to the cooled mixture. After 30 min, NaOAc (1.64 g, 0.02 mol) was added and the stirring continued overnight at room temperature. A red-brown solid was collected, washed with H_2O, and purified by column chromatography on alumina (CH_2Cl_2) to give a bright orange waxy solid: yield, 9 g (31%); ^1H NMR ($CDCl_3$) δ 3.45 (m, 4 H, CH_2), 3.80 (m, 2 H, CH_2), 3.90 (m, 2 H, CH_2), 6.98 (d, 2 H, Ar), 7.95 (m, 6 H, Ar), 10.07 (s, 1 H, CHO); mass spectrum, *m/e* (rel intensity) 390 (100), 257 (75). Anal. Calcd for $C_{19}H_{17}N_4O_2F_3$: C, 58.5; H, 4.4; N, 14.4. Found: C, 58.4; H, 4.4; N, 14.4.

1-[(4-[4-(Trifluoroacetyl)piperazinyl]phenyl)azo]-4-[2-(1,3-dioxolanyl)]benzene, 6c. Compound **6b** (0.5 g, 1.3 mmol) was dissolved in benzene (10 mL) with heating, ethylene glycol (0.2 g, 3.2 mmol) and pyridinium hydrochloride (0.05 g, 0.4 mmol) were added, and the solution was refluxed overnight. The solvent was evaporated, and the residue was purified by column chromatography on silica gel (EtOAc (75)/hexane (25%)) to yield 0.4 g (71%) of "metallic" gold solid: ^1H NMR ($CDCl_3$) δ 3.45 (m, 4 H, CH_2N), 3.80 (m, 2 H, CH_2N), 3.87 (m, 2 H, CH_2N), 4.07 (m, 2 H, CH_2O), 4.15 (m, 2 H, CH_2O), 5.88 (s, 1 H, CH), 6.98 (d, 2 H, Ar), 7.60 (d, 2 H, Ar), 7.88 (m, 4 H, Ar).

1-([(4-Piperazinyl)phenyl]azo)-4-[2-(1,3-dioxolanyl)]benzene, 7c. NaOH (0.02 g, 0.35 mmol) was added to **6c** (0.15 g, 0.3 mmol) in EtOH (50 mL) and the solution stirred at room temperature for 2 h. The EtOH was evaporated, CH_2Cl_2 added, and the solution washed with H_2O (pH > 7). The organic layer was dried and evaporated to give an orange solid which was used without further purification: yield, 0.06 g (52%); ^1H NMR ($CDCl_3$) δ 3.05 (m, 4 H, CH_2N), 3.25 (m, 4 H, CH_2N), 4.07 (m, 2 H, CH_2O), 4.15 (m, 2 H, CH_2O), 5.90 (s, 1 H, CH), 6.98 (d, 2 H, Ar), 7.60 (d, 2 H, Ar), 7.88 (m, 4 H, Ar).

1-(2-Cyano-3-[([4-(*N*,*N*-dimethylamino)phenyl]azo)phenyl]propenoyl)-4-[4-(1,3-dioxolanyl)phenyl]piperazine,

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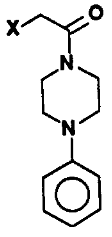
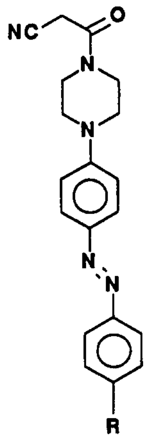
1c. Compounds 4 (0.2 g, 0.6 mmol) and 7c (0.2 g, 0.6 mmol) were reacted with DCC (0.12 g, 0.6 mmol) in CH_3CN (10 mL)/dimethyl sulfoxide (DMSO, 10 mL) at room temperature for 72 h. The CH_3CN was evaporated, and CH_2Cl_2 and H_2O were added to the reaction mixture. The organic layer was separated, dried, and evaporated, and purification of the residue was attempted by using TLC (silica gel, CH_2Cl_2). NMR suggested that some of the desired product may have been formed but only as a minor product: GPC retention volume, 6.4 mL.

***N,N*-Dimethyl-2-cyano-3-([(4-[4-(trifluoroacetyl)-piperazinyl]phenyl)azo]phenyl)propenonamide, 6d.** *N,N*-Dimethylcyanoacetamide[11] (0.1 g, 0.9 mmol), **6b** (0.1 g, 0.3 mmol), and pyridine (0.02 g, 0.3 mmol) were placed in a test tube and heated at 55 °C for 2 h and then let stand overnight at room temperature. The reaction mixture was triturated with MeOH, and the product was collected and dried under vacuum, to give **6d** in 85% yield: mp 207–210 °C; ^1H NMR ($CDCl_3$) δ 3.08 (s, 3 H, CH_3), 3.22 (s, 3 H, CH_3), 3.45 (m, 4 H, CH_2), 3.80 (m, 2 H, CH_2), 3.88 (m, 2 H, CH_2), 7.02 (d, 2 H, Ar), 7.80 (s, 1 H, =CH), 7.99 (m, 4 H), Ar), 8.04 (d, 2 H, Ar); mass spectrum, *m/e* (rel intensity) 484 (75), 257 (100), 118 (60).

1-(Chloroacetyl)-4-phenylpiperazine, 8a. *N*-Phenylpiperazine (16.2 g, 0.1 mol) and triethylamine (10.1 g, 0.1 mol) were dissolved in CH_2Cl_2 (150 mL) and cooled to 0 °C with stirring. Chloroacetyl chloride (11.3 g, 0.1 mol) in CH_2Cl_2 (50 mL) was added dropwise over 30 min, and the stirring at 0 °C continued for 2 h. The reaction mixture was washed with 10% $NaHCO_3$ to pH 7 and finally with water. The CH_2Cl_2 layer was dried (Na_2SO_4), filtered, and evaporated to give **8a** which was used without further purification: yield, 23.5 g (100%); ^1H NMR ($CDCl_3$) 3.20 (m, 2 H, CH_2N)8 3.25 (m, 2 H, CH_2N), 3.65 (m, 2 H, CH_2N), 3.78 (m, 2 H, CH_2N), 4.10 (s, 2 H, CH_2), 6.95 (m, 3 H, Ar), and 7.28 (m, 2 H, Ar).



8 a. X = Cl
b. X = CN



9 a. R = NO_2
b. R = CHO

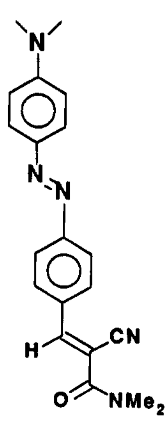
1-(Cyanoacetyl)-4-phenylpiperazine, 8b. Tetrabutylammonium cyanide[12] (Fluka 26.8 g, 0.1 mol) in CH_2Cl_2 (250 mL, anhydrous) was added dropwise over 1 h to a solution of **8a** (12 g, 0.05 mol) in CH_2Cl_2 (250 mL) cooled to 0 °C and the reaction mixture stirred an additional 2 h at 0 °C. After washing with aqueous 5% HCl three times to remove tributylamine and excess CN^- (CAUTION) and once with water, the CH_2Cl_2 layer was dried over $MgSO_4$, filtered, and evaporated. The brown oil solidified after pumping overnight under vacuum and was used without further purification: yield 10 g (87%); ^1H NMR ($CDCl_3$) δ 3.25 (m, 2 H, CH_2N), 3.30 (m, 2 H, CH_2N), 3.60 (s, 2 H, CH_2), 3.68 (m, 2 H, CH_2N), 3.85 (m, 2 H, CH_2N), 6.95 (m, 3 H, Ar), 7.35 (m, 2 H, Ar); mass spectrum, *m/e* (rel intensity) 229 (100), 161 (35), 132 (70), 105 (50); GPC retention volume (100-Å μ-Spherogel, 5% DMSO/95% CH_2Cl_2), 7.5 mL. Anal. Calcd for $C_{13}H_{15}N_3O$: C, 68.1; H, 6.6; N, 18.3. Found: C, 68.0; H, 6.6; N, 18.0.

1-(Cyanoacetyl)-4-([(4-nitrophenyl)azo]phenyl)piperazine, 9a. In a procedure similar to that described above for the preparation of **6a**, **8b** (0.5 g, 2.2 mmol) was reacted with 4-nitrobenzenediazonium tetrafluoroborate to give **9a** in 90% yield after purification by column chromatography (silica gel, CH_2Cl_2/hexane): ^1H NMR (CD_3CN) δ 3.50 (m, 6 H, CH_2N), 3.70 (m, 2 H, CH_2N), 3.75 (s, 2 H, CH_2), 7.03 (d, 2 H, Ar), 7.90 (m, 4 H, Ar), 8.30 (d, 2 H, Ar); GPC retention volume, 6.8 mL.

1-(Cyanoacetyl)-4-([(4-formylphenyl)azo]phenyl)-piperazine, 9b. In a procedure similar to that described above for the preparation of **6b**, **8b** (2.3 g, 0.01 mol) was reacted with 4-benzaldehydediazonium salt, taking care to maintain the temperature below 10 °C at all times. The red solid was purified by trituration with MeOH (90%)/H_2O (10%), collected, and dried to give **9b** in 39% yield (1.4 g): ^1H NMR (CD_3CN) δ 3.50 (m, 6H, CH_2N), 3.70 (m, 2 H, CH_2N), 3.72 (s, 2 H, CH_2), 7.07 (d, 2 H, Ar), 7.95 (d, 2 H, Ar), 7.97 (d, 2 H, Ar), 8.03 (d, 2 H, Ar), 10.05 (s, 1 H, CHO); mass spectrum, *m/e* (rel intensity) 361 (100), 228 (92); GPC retention volume (100-Å μ-Spherogel, 5% DMSO/95% CH_2Cl_2), 7.0 mL.

Poly[1-(cyanoacetyl)-4-([(4-formylphenyl)azo]phenyl)-piperazine], 2. Compound **9b** (0.5 g, 1.4 mmol) was "dissolved" in a minimum of NMP (1 mL). A drop of piperidine was added and the solution stirred at 100 °C overnight under N_2. The NMP was removed under vacuum to yield a red–brown solid that was collected after triturating with CH_2Cl_2. GPC retention volume (100-Å μ-Spherogel, 5% DMSO/95% CH_2Cl_2), 5.5–6.9 mL.

***N,N*-Dimethyl-2-cyano-3-[4-([4-(*N,N*-dimethylamino)-phenyl]azo)phenyl]propenamide, 10.** *N,N*-Dimethylcyanoacetamide[11] (0.56 g, 0.005 mol), 4-([4-(*N,N*-dimethylamino)-phenyl]azo)benzaldehyde (1.26 g, 0.005 mol), and pyridine (0.4 g, 0005 mol) were stirred in a flask overnight at 80 °C. The pyridine was removed under vacuum, and the red solid was purified by column chromatography on silica gel, eluting with CH_2Cl_2: yield, 1.1 g (63%); ^1H NMR ($CDCl_3$) δ 3.08 (br s, 3 H, CH_3), 3.13 (s, 6 H, CH_3), 3.25 (br s, 3 H, CH_3), 6.79 (d, 2 H, ArH), 7.80 (s, 1 H, =CH), 7.92 (d, 4 H, ArH), 8.04 (d, 2 H, ArH); mass spectrum, *m/e* (rel intensity) 347 (84), 120 (100). Anal. Calcd for $C_{20}H_{21}N_5O$: C, 69.14; H, 6.09; N, 20.16. Found: C, 69.06; H, 6.17; N, 19.91.



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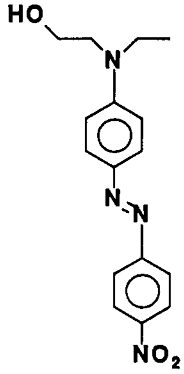

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Results

Amides via Coupling. We have found that the coupling of a carboxylic acid to an amine using carbonyldiimidazole (CDI) as the coupling agent[8] is not applicable to azo cinnamate dyes. However, by using dicyclohexylcarbodiimide (DCC), we were able to prepare **3** in 30% yield from **4** and *N*-phenylpiperazine (method A). The major product isolated from this reaction was **5**, apparently formed by the hydrolysis of **4** in the reverse Knoevenagel sense.

Several phenylpiperazine derivatives, (**7a,c,d**), each having an azo linkage and a potential electron acceptor, were targeted in the hope of coupling them to **4** using DCC. Because we have found the nitrogen of the secondary amine to be reactive during electrophilic substitution, we first prepared the *N*-(trifluoroacetyl) (TFA) derivatives **6a–d**, as a means of protecting the nitrogen during subsequent reactions. We have previously shown[8] the TFA group to be a good protecting group for amines of this type.

The piperazinyl azo dyes **6a,b** were prepared by standard azo coupling[9] of the 4-nitrobenzene- and benzaldehydediazonium salts, respectively, to 1-(trifluoroacetyl)-4-phenylpiperazine. The protected aldehyde **6c** was synthesized by the acid-catalyzed reaction of **6b** with ethylene glycol. This protecting group can be removed under mildly acidic conditions to restore the reactive aldehyde. Compound **6d** was obtained from the Knoevenagel reaction of **6b** with *N,N*-dimethylcyanoacetamide.

The TFA group can be removed from the piperazine dyes under moderately basic conditions. Tetrabutylammonium hydroxide was used to prepare **7a**; however, the pH had to be carefully balanced in the workup to avoid protonation of the piperazine nitrogen. Also, the tributylamine impurity from the base was difficult to remove completely from the product. In cases where the protonated intermediate was isolated because of difficulties in balancing the pH, additional reflux of the solid with alcoholic NaOH was necessary to liberate the free base.

Alcoholic NaOH was found to be effective for removal of the protecting group and for avoiding protonation in the conversion of **6c** to **7c** and was used for removing the TFA groups in subsequent reactions. The amide group of **6d** was more sensitive to base and, therefore, more easily removed then the TFA group, and **7d** could not be prepared in this manner.

Once the deprotected piperazine derivatives had been obtained, several unsuccessful attempts were made to couple **4** and **7a** using DCC under a variety of reaction conditions. The two starting materials had different solubilities, necessitating dual-solvent systems. A 1:1 "salt" was isolated when CH_2Cl_2/CH_3CN was the reaction medium. Compound **5** was also identified in the filtrate by NMR. In other solvents tried, unreacted **4** was recovered, as well as a byproduct which may be a dicyclohexylurea adduct. Protected aldehyde **7c** probably underwent the desired coupling with **4** to some extent, based on TLC and NMR evidence, but the reaction mixture contained numerous side products.

Compound **1a** was successfully prepared, albeit in unsatisfactory yield, by reaction of **3** with 4-nitrobenzenediazonium tetrafluoroborate under standard azo coupling conditions. NMR and GPC data were consistent with the structure **1a**.

Amides via Knoevenagel Condensation. Because of the difficulties in the preparation of the substituted piperazines and in the DCC reaction itself, we attempted to prepare dipolar bis azo dyes by using the Knoevenagel reaction. Compound **5**[10] was used as the top half of the "dimers" in the reactions discussed below. It was prepared in large quantities by azo coupling of benzaldehydediazonium salt to dimethylaniline and was readily purified. Preparation of the various cyanomethylene compounds could also be readily accomplished.

Compound **8b** was initially prepared by the reaction[11] of ethyl cyanoacetate with *N*-phenylpiperazine, but yields were inconsistent and the product could not be easily purified for further use. We found that **8b** could best be prepared by reaction of chloroacetyl chloride with *N*-phenylpiperazine, to give **8a** in ~100% yield, followed by reaction with tetrabutylammonium cyanide[12] to give **8b** in 87% yield. This material crystallized and could be used without further purification. The reaction of **5** and **8b** in ethanol with piperidine catalyst (method B) gave **3** in improved yields over method A.

Compound **8b** also served as the starting material for the other cyanomethylene compounds. Compounds **9a,b** were synthesized by azo coupling of the appropriate diazonium salts to **8b**. The products were isolated as solids, and care was taken to remove all traces of acid before further reaction. These cyanomethylene derivatives were also prepared by reaction of the piperazine azo dyes **7a,c** with chloroacetyl chloride followed by reaction with tetrabutylammonium cyanide. However, we found it more convenient to prepare **8b** in large quantities and then do the azo couplings in order to minimize the number of reactions on the azo dyes.

The dipolar bis azo dye **1a** was prepared in acceptable yields (37%) by the Knoevenagel reaction of **5** with **9a** (method B). After exploring various experimental conditions, we found that the reaction proceeded best at 100 °C with piperidine as catalyst, using a minimum of *N*-methyl-2-pyrrolidinone (NMP) as solvent. The pure product was isolated after three dissolution (CH_2Cl_2)/trituration (CH_3CN) cycles, as described in the Experimental Section.

By use of a similar procedure, **9b** underwent a self-condensation to give oligomer **2**, which was characterized by GPC. Analysis of the oligomer was carried out on a 100-Å μ-Spherogel column using a 5% DMSO/95% CH_2Cl_2 solvent system. An uneven distribution of sizes corresponding to oligomers of three to nine units was observed, based on extrapolation of the line defined by the retention volumes of compounds **8b**, **9b**, and **1a**, run under identical conditions.

Dipole Moments. The dipole moments of **1**, **10**, a model for the top half of **1**, and **11**, a model for the bottom half of **1**, were measured in $CHCl_3$. These compounds were not sufficiently soluble in dioxane to allow its use for these determinations. Because of the low concentrations used for the experimental solutions, interactions of the substrates with the capacitor surfaces that are only apparent at low concentrations and the higher dielectric loss of $CHCl_3$ relative to dioxane contribute higher uncertainties to the results then would have been expected from dioxane determinations. We estimate the 95% confidence limit of our dielectric data to be 1 D. However, most of the systematic uncertainty should be common to the three compounds and not greatly hinder comparisons among them. The experimental data are listed in Table I.

Discussion

Amides via Coupling. We have previously shown that CDI promotes the condensation of 2-cyano-3-[4-(*N,N*-dimethylamino)phenyl]-1-propenoic acid and *N*-phenylpiperazine to an amide.[8] However, attempts to perform the analogous reaction on **4** were unsuccessful. The CDI reaction is thought to proceed by nucleophilic attack of the carboxylic acid on the carbonyl carbon of CDI, loss of CO_2 to produce an acylimidazole intermediate, and substitution of the free amine for the remaining imidazole on the acylimidazole intermediate.[13] However, the electron-withdrawing properties of the azo group may disfavor this mechanism by lowering the nucleophilicity of the carboxylic acid and making nucleophilic addition of adventitious water to the carbon–carbon double bond, the first step of a reverse Knoevenagel reaction, more favored. Attempts to allow longer times for acylimidazole formation before amine addition or to add base in order to favor coupling over nucleophilic displacement of the CN were unsuccessful.

Therefore, DCC, a coupling agent that reacts via a different mechanism,[14] was used. The DCC reaction is initiated by protonation of a carbodiimide nitrogen followed by conversion of the carboxylic acid to an *O*-acylurea intermediate that then reacts with the amine, eliminating dicyclohexylurea. The reaction of **4** with *N*-phenyl-

Table I. Dipole Moments on Chromophores in $CHCl_3$ Solution

compd	μ, D	concn range,[a] M	correlation coeff[b]
1	13.0	0.00094–0.0023	0.989
10	6.7	0.0027–0.0060	0.983
11	7.1	0.0033–0.017	0.998

[a] Of solutions used for dielectric constant measurements. [b] Of plots of dielectric constant vs weight fraction of solute.

piperazine using DCC gives **3** in ~30% yield and was expected to be a model for the reaction of **4** with more complex piperazine derivatives, **7a–d**. Such reactions would have provided one means of linking dipolar azo monomer units, head-to-tail, by coupling a carboxylic acid to a secondary amine to give an amide.

Attempts to couple the piperazine azo dyes to carboxylic acid **4** were unsuccessful. In the case of **7a**, no convenient common solvent could be found for the two components. Side reactions of the azo moiety (especially in the case of **7c**) or of the electron acceptor group may have competed with the formation of the DCC adduct.

Amides via Knoevenagel Condensation. Because of the difficulties in the preparation of the free piperazine azo dyes and in the DCC reaction itself, we investigated another approach to linking these dipolar azo monomer units. Having successfully employed the Knoevenagel reaction to convert aldehyde moieties into cyanovinyl groups, we extended this reaction[15] to serve as the key bond-forming step in linking the dipolar azo dyes. Although standard Knoevenagel conditions (EtOH, piperidine) were sufficient to prepare **3** in improved yields over method A, limited solubilities prevented us from using these conditions for the azo-substituted cyanomethylenes. Only by heating the reagents in a minimum amount of NMP with piperidine were we able to obtain the "dimer" **1a** and the "polymer" **2**. Under these specific conditions, the difficulties imposed by the azo groups because of aggregation and changes in the electron distribution at the reactive sites were largely overcome.

Dipole Moments. The dipole moment of **1a** may be compared with a theoretical value for the moment of its two segments as an uncorrelated pair. The orientational dielectric susceptibility of such a pair of dipoles with magnitudes μ_1 and μ_2 would correspond to a dipole moment of $(\mu_1^2 + \mu_2^2)^{1/2}$. This is equivalent to the two segments held at 90° relative orientations. Because the piperazinamide linkage enforces a 110° angle between segments,[8] the dipole moment of **1a**, 13 ± 1 D, is larger than $(6.7^2 + 7.1^2)^{1/2}$, which equals 9.8 ± 1.3 D. Thus, enhancement of the dipole moment additivity, observed as a dielectric response in a dimer solution greater than what would be expected from a solution of the monomers at the same concentration, which should translate into enhanced electric field orientability for poled nonlinear optical materials, has been extended from simple disubstituted benzenes to azo dyes connected by the piperazinamide linkage. If the extended conformation can be maintained in higher oligomers such as **2**, the enhancement in the oligomers should be considerably larger.

Conclusion

We have evaluated several different approaches to the synthesis of highly dipolar pseudodimers and polymers containing azo linkages. While standard acid–amine coupling reactions are only occasionally sucessful in the presence of the azo groups, the Knoevenagel reaction, under specific conditions, generates the desired azo–amide oligomers, which possess significantly additive dipole moment vectors in their extended conformations. The nonlinear optical and dielectric properties of these materials are currently being evaluated.

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