

Head-to-Tail Assemblies of Dipolar, Piperazine-Linked Chromophores: Synthesis, X-ray Structure, and Dielectric Characterization

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Received September 28, 1988

Abstract: A dimer and a mixture of oligomers of acceptor-substituted anilines were prepared, either by Knoevenagel condensation of substituted cyanoacetyl piperazines with *p*-aminobenzaldehydes or by carbonyldiimidazole-promoted coupling of phenyl piperazines with *p*-aminocyanocinnamic acids. The resulting oligomeric amidopiperazines possess significantly additive molecular moments when in extended conformations and therefore are potentially valuable for the fabrication of polymer films containing electric field oriented chromophores, such as required for second-order nonlinear optics. The dimer is conformationally defined, and X-ray structural analysis of a model compound confirmed the stereochemistry and bond angles at the amide linkage. The enforced extended conformation of the dimer resulted in an enhanced dipole moment relative to the constituent monomers and raises the possibility of further enhancements in extended higher oligomers.

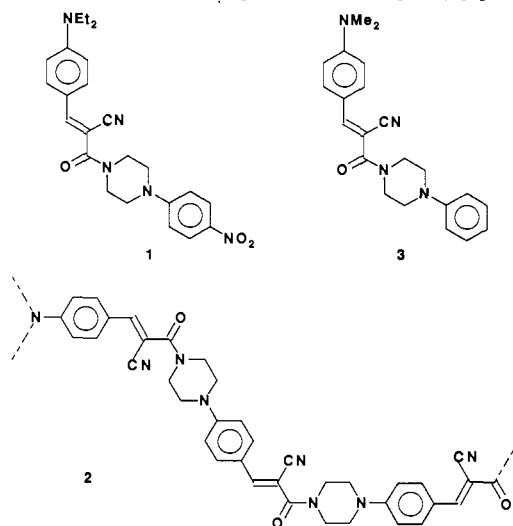
Organic polymers containing dissolved¹ or covalently attached² chromophores are under widespread investigation because of their nonlinear optical and electronic properties. Imparting a net directionality to the chromophores, for example, by electric field poling, results in materials exhibiting pyroelectric³ and electrooptical⁴ behavior. Although poling of noninteracting dipolar chromophores induces a useful degree of orientation, it would be desirable to increase this orientation further.

Several means of doing so have been considered. An approach that was successful in one special case⁵ was to pole noncentrosymmetric aggregates of a dye in a polymer host. Ferroelectric crystalline^{1b} phases of polymer hosts have been proposed to favorably influence the ordering of dyes dissolved therein. Dipolar molecules included in liquid crystals^{2a,b} have been extensively examined for nonlinear optics. In ordinary nematics and smectics, some advantage is gained by drastically reducing the population of electroactive species lateral to the poling field, although a large fraction of the molecules are opposed to the field.

One method for greatly increasing the effective dipole moment, and therefore the poling-induced alignment, of an assembly of dyes is to connect them in a head-to-tail arrangement as part of a polymer backbone, as illustrated in Figure 1. Polyesters of this type have been reported, containing either highly dipolar and hyperpolarizable but relatively intractable monomers⁶ or else much less hyperpolarizable and somewhat more tractable monomers⁷ copolymerized with flexible polymethylene subunits. Other polymers incorporating extensively conjugated π systems in the

main chain have not been directional.⁸

This paper describes the synthesis of a dimer and an oligomeric mixture, **1** and **2**, based on acceptor-substituted phenyl piperazines.



One of the nitrogens in each piperazine is envisioned as an electron donor in a dipolar π system, while the other is part of a conformationally defined linking group. All nitrogens are tertiary in these compounds, leaving no residual, hydrogen bondable NH groups that could decrease tractability. The piperazinyl portion of the molecules induces little change in the direction of the dipolar oligomer backbone; in particular, the linkage prevents antiparallel alignment of adjacent segments. The combination of X-ray crystallographic and solution dielectric characterization of compounds with the dimeric structure validates the use of dielectric measurements to observe dipole additivity and confirms that rational increases in total dielectric susceptibility may be observed in head-to-tail polymers versus ensembles of the constituent monomers even when the degree of "polymerization" is only 2.

Results

Dimer 1 and Model Compound 3. Two different reactions were employed as the key bond-forming reactions for the construction of the cyanopropenoamide linkage in these compounds. The first (eq 1) was the Knoevenagel condensation of cyanoacetamide **4** with a *p*-aminobenzaldehyde, under the standard conditions of

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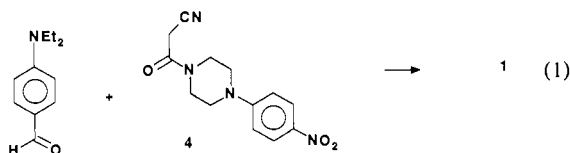
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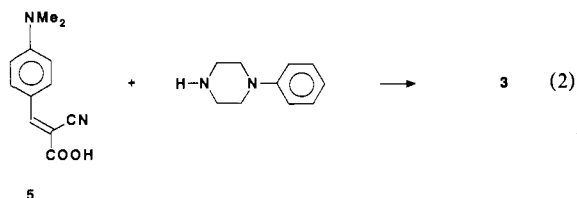
(6) Green, G. P.; Hall, H. K., Jr.; Mulvaney, J. E.; Noonan, J.; Williams, D. J. *Macromolecules* **1987**, *20*, 716.

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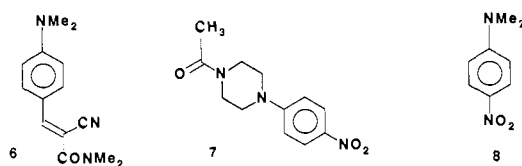


alcohol solvent and piperidine catalyst. The second (eq 2) was the carbonyldiimidazole-mediated amide coupling of 4-phenylpiperazine with *p*-amino- α -cyanocinnamic acid **5**. Both products were obtained analytically pure after chromatography and/or crystallization. It was not possible to synthesize cyanocinnamate esters⁷ by these methods.



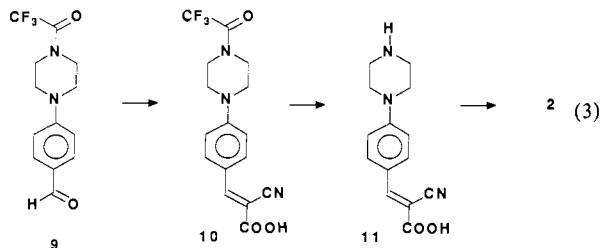
The X-ray structure of **3** is shown in Figure 2; bond lengths and angles of non-hydrogen atoms are listed in Tables I and II. The angle between the C₄-C₇ bond and the C₉-N₃ bond is 125°. Rotation about the C₈-C₉ bond in solution would produce a range of angles between the segments of 102–132°. If the piperazine ring remains in a symmetrical chair form, this rotation is the only conformationally significant degree of freedom. The piperazine ring of **3** does deviate somewhat from a perfect chair, however, resulting in a slightly decreased segment–segment angle. It is reasonable to expect the structure of an analogue of **3**, such as **1**, to be more symmetrical and extended because of increased planarity at N₄. Allowing for variation in the piperazine conformation and the possibility that the dipole moment of the cyanovinyl-substituted chromophore is not coincident with the C₄-C₇ axis enables one to estimate the segmental angle in **1** to be close to 110°.

The dipole moments of **1**, **6**, a model for the “top half” of **1**, and two models for the “bottom half” of **1**, **7** and **8**, were measured



in dioxane solution and are tabulated along with relevant experimental parameters in Table III. The error due to scatter of the data points is only on the order of 0.1 D, while any systematic errors, which are probably on the order of 0.3 D, should be common to the three compounds and not hinder comparisons among them.

Oligomer 2. The sequence for the synthesis of **2** is shown in eq 3. The most efficient series of reactions was to protect the free NH of *N*-phenylpiperazine as the trifluoroacetamide and then conduct a Vilsmeier formylation⁹ on the protected derivative, condense the resulting benzaldehyde with cyanoacetic acid,¹⁰ and deprotect to form **11**. When the Vilsmeier reaction was per-



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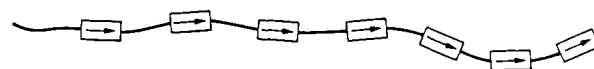


Figure 1.

Table I. Intramolecular Distances Involving the Non-Hydrogen Atoms

atom	distance ^a	atom	distance ^a		
O(1)–C(9)	1.220 (9)	C(4)–C(5)	1.38 (1)		
N(1)–C(1)	1.36 (1)	C(4)–C(7)	1.46 (1)		
N(1)–C(22)	1.44 (1)	C(5)–C(6)	1.38 (1)		
N(1)–C(21)	1.48 (1)	C(7)–C(8)	1.36 (1)		
N(2)–C(10)	1.14 (1)	C(8)–C(10)	1.43 (1)		
N(3)–C(9)	1.374 (9)	C(8)–C(9)	1.51 (1)		
N(3)–C(11)	1.46 (1)	C(11)–C(12)	1.52 (1)		
N(3)–C(14)	1.461 (8)	C(13)–C(14)	1.54 (1)		
N(4)–C(15)	1.42 (1)	C(15)–C(20)	1.39 (1)		
N(4)–C(13)	1.44 (1)	C(15)–C(16)	1.39 (1)		
N(4)–C(12)	1.475 (8)	C(16)–C(17)	1.38 (1)		
C(1)–C(2)	1.39 (1)	C(17)–C(18)	1.38 (1)		
C(1)–C(6)	1.42 (1)	C(18)–C(19)	1.37 (1)		
C(2)–C(3)	1.37 (1)	C(19)–C(20)	1.38 (1)		
C(3)–C(4)	1.43 (1)				
atom	distance ^b	ADC(*)	atom	distance ^b	ADC(*)
O(1)–C(13)	3.477 (8)	45 501	N(2)–C(21)	3.54 (1)	65 502
O(1)–C(21)	3.53 (1)	54 502	N(2)–C(22)	3.59 (1)	65 502
O(1)–C(22)	3.53 (1)	54 502	C(1)–C(3)	3.48 (1)	2
O(1)–C(20)	3.60 (1)	45 501	C(11)–C(19)	3.51 (1)	46 501
N(2)–C(7)	3.40 (1)	56 501	C(11)–C(18)	3.59 (1)	46 501
N(2)–C(9)	3.50 (1)	56 501			

^a Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses. ^b Contacts out to 3.60 angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table II. Intramolecular Bond Angles Involving the Non-Hydrogen Atoms

atom	angle ^a	atom	angle ^a
C(1)–N(1)–C(22)	122.4 (7)	C(7)–C(8)–C(10)	124.0 (8)
C(1)–N(1)–C(21)	121.1 (7)	C(7)–C(8)–C(9)	115.6 (8)
C(22)–N(1)–C(21)	116.3 (6)	C(10)–C(8)–C(9)	120.1 (8)
C(9)–N(3)–C(11)	117.5 (7)	O(1)–C(9)–N(3)	122.6 (7)
C(9)–N(3)–C(14)	125.2 (6)	O(1)–C(9)–C(8)	120.3 (7)
C(11)–N(3)–C(14)	111.5 (6)	N(3)–C(9)–C(8)	116.9 (7)
C(15)–N(4)–C(13)	115.6 (6)	N(2)–C(10)–C(8)	178 (1)
C(15)–N(4)–C(12)	114.7 (7)	N(3)–C(11)–C(12)	110.8 (7)
C(13)–N(4)–C(12)	111.7 (6)	N(4)–C(12)–C(11)	109.1 (7)
N(1)–C(1)–C(2)	121.6 (8)	N(4)–C(13)–C(14)	111.5 (6)
N(1)–C(1)–C(6)	121.5 (8)	N(3)–C(14)–C(13)	110.9 (7)
C(2)–C(1)–C(6)	116.9 (7)	C(20)–C(15)–C(16)	116.6 (8)
C(3)–C(2)–C(1)	121.7 (8)	C(20)–C(15)–N(4)	122.2 (7)
C(2)–C(3)–C(4)	120.9 (8)	C(16)–C(17)–N(4)	121.1 (6)
C(5)–C(4)–C(3)	117.5 (7)	C(17)–C(16)–C(15)	121.7 (7)
C(5)–C(4)–C(7)	127.3 (8)	C(16)–C(17)–C(18)	120.8 (8)
C(3)–C(4)–C(7)	115.2 (7)	C(19)–C(18)–C(17)	118.4 (9)
C(6)–C(5)–C(4)	121.2 (8)	C(18)–C(19)–C(20)	121.3 (7)
C(5)–C(6)–C(1)	121.4 (8)	C(19)–C(20)–C(15)	121.2 (8)
C(8)–C(7)–C(4)	130.9 (8)		

^a Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Table III. Dipole Moments of Chromophores in Dioxane

compd	μ , D	concn range, ^a M	correlation coeff ^b
1	9.1	0–0.023	0.99997
6	5.3	0–0.051	0.9995
7	4.8	0–0.050	0.9992
8	6.8	0–0.075	0.9998

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

formed on *N*-*tert*-butoxycarbonyl, or *N*-triphenylmethyl-protected reagent, mixtures of C- and N-formylated products were obtained. Though much less convenient, these mixtures could also be carried through to eventually obtain **11**. Removal of the trifluoroacetyl

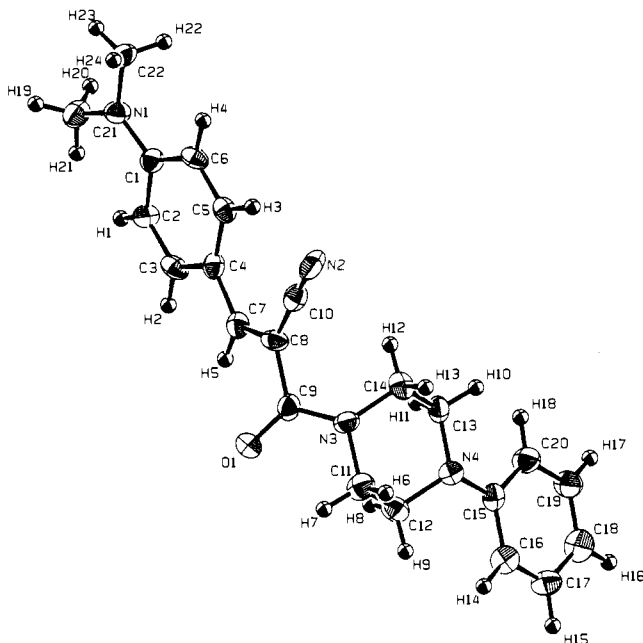


Figure 2.

group was effected by reaction with Bu_4NOH at room temperature. After workup with HI to increase the organic extractability of the Bu_4N salt, **11** was filtered from the aqueous layer and used, after drying, without further purification.

Oligomer **2** was obtained in good yield from the CDI coupling of **11**. The oligomerization was modeled by the condensation of **5** with *N*-phenylpiperazine as shown in eq 2. The weight-average degree of oligomerization was 12 and may have been limited by the precipitation of the oligomer from the reaction mixture. NMR spectroscopy again supported the assigned structure of the oligomer. In particular, the ^{13}C spectrum of the oligomer showed a clear amide resonance at 169 ppm but no urea resonance analogous to that of carbonylbis(4-phenylpiperazine), which occurs at 162.5 ppm.¹¹ Unfortunately, the insolubility of **2** in any but the most polar solvents precluded the facile measurement of its effective dipole moment.

Discussion

The dipole moment of **1** may be viewed as the vector sum of the dipole moments of its "halves". Compound **6** is obviously a proper model for the top half, while the two nitroanilines **7** and **8** probably represent extreme values for the bottom half, depending on the component of the amide moment of **1** that is opposite to the major moments. Assuming that one molecule of **6** and one molecule of either **7** or **8** add vectorially to give the total dipole moment of **1**, the angle between the halves is calculated to be 97° or 128° , respectively, bracketing the value predicted from crystallography and molecular models.

Another way to examine the dipole moment data is to compare the measured moment of the correlated dipoles that comprise **1** with a theoretical dielectric polarization that would have been observed for the same chromophores added together as an uncorrelated pair. If the pair of moments has magnitudes of μ_1 and μ_2 , the theoretical value for their combined contributions to the polarization of a solution containing both, expressed as the moment of an uncorrelated pair, equivalent to fixing the pair at right angles, is $(\mu_1^2 + \mu_2^2)^{1/2}$. These theoretical values using the measured moments of the model for the top segment and each of the two bottom segments (separately) are 7.1 and 8.6 D. Thus, **1** displays increased dielectric orientational polarizability corresponding to a dipole moment increment of 0.5–2.0 D over an appropriate reference state. This is the first such enhancement that has been obtained in a chromophore assembly relevant to nonlinear optics

and that has been rationalized on the basis of conformational analysis. If an extended conformation could be maintained, enhancements for higher oligomers should be larger, since in favorable cases, the enhancement is in theory a linear function of the degree of polymerization.⁷ However, if a longer oligomer or polymer adopts a helical or doubled-back conformation, the enhancement would not increase as greatly with the length of the macromolecule.

Carbonyldiimidazole is a widely used reagent for the synthesis of biologically relevant amides, including polypeptides.¹² Except for one previous instance,¹³ its use in abiotic polymer chemistry has been limited to monomer preparation,¹⁴ polymer modification,¹⁵ and polycarbonate synthesis,¹⁶ where the carbonyl group of the carbonate is supplied by CDI. It appears from this work that CDI is a worthwhile reagent for the polymerization of polar amino acids, particularly because these monomers are insoluble in the relatively nonpolar solvents that are typically required for other coupling reagents such as EEDQ. As such, CDI represents a valuable alternative to previous methods for the synthesis of head-to-tail polymers that may find applications in nonlinear optics.¹⁷

In its stretched-out conformations, the oligomer **2** fits the generic structure illustrated in Figure 1 and incorporates moieties with larger expected hyperpolarizabilities¹⁸ and more rigid subunits than did previously synthesized, tractable, head-to-tail polymers. Although the exact equilibrium conformation remains to be elucidated, the new oligomer possesses few conformational degrees of freedom. This relatively rigid material could in principle be made more flexible by preparing it as a blocky copolymer with aliphatic ω -amino acids, thereby increasing its solubility and the limiting degree of polymerization and possibly rendering it amenable to solution-phase dielectric characterization as was described for **1**.

Several synthetic procedures are described in this paper in addition to the polymerizations. These include the deprotection–isolation of a zwitterionic amino acid employing Bu_4NOH and HI as basic and acidic reagents, enabling the salts to be removed from the hydrophilic products by washing with a hydrophobic solvent, aromatic formylation in the presence of a protected amine, Knoevenagel reactions for the preparation of highly functionalized cyanocinnamamides, and amine deprotection in the presence of the cyanocinnamic acid group. Taken together, these reactions will make possible the synthesis of specific oligomers of chromophoric molecules such as those discussed here, from which detailed conformational data may also be obtained.

Experimental Section

General Procedures. Reagents were used as received; solvents were anhydrous. NMR spectra, expressed as ppm relative to internal Me_4Si were obtained on a Bruker AM 360 spectrometer. UV–visible spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer. Polymer molecular weights were obtained by gel permeation chromatography (GPC) relative to polystyrene standards. GPC measurements were performed on a Beckman HPLC system with a Waters Model 481 detector using a μ -spherogel column (500 Å). A 5% DMSO/ CH_2Cl_2 solvent system was used. The polystyrene standards were detected at 270 nm whereas the polymers were detected at 500 nm. Mass spectra were recorded on a Hewlett-Packard 5985B spectrometer. Elemental analyses were performed by Galbraith Laboratories.

Dipole moments were determined by measuring the capacitance of serially diluted dioxane solutions in a cell consisting of a 25-mm-diameter

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tube with platinum sputtered on the inner surface and a 22-mm-diameter insert with platinum sputtered on the outer surface. The actual dielectric region was 4.6 cm high, separated by thin, metal-free rings from grounded regions above and below. Data were obtained with an Andeen-Hagerling 1-kHz self-balancing bridge, in which effects of dielectric loss are well isolated from the capacitance measurement. Dielectric constants of pure solvents observed in this apparatus were within 0.5% of generally accepted values. Dipole moments μ were calculated by solving eq 4¹⁹ where $[s_i]$ is the concentration of the i th species expressed

$$\frac{\epsilon - 1}{4\pi} = \sum_i [s_i] \left(\alpha f_i + \frac{\mu_i^2 f_i'}{3kT} \right) \quad (4)$$

in terms of its weight fraction w , α is the linear polarizability, and f_i and f_i' are local field factors, differentiated with respect to solute mass fraction, using the slopes of plots of the dielectric constants versus mass fraction as the values for $d\epsilon/d(\text{mass fraction})$, assuming Onsager local fields²⁰ and incorporating reliable estimates for solute contributions to the density and linear polarizability of the solutions.

1-(Cyanoacetyl)-4-(4-nitrophenyl)piperazine (4). Tetrabutylammonium cyanide (Fluka, 19 g, 0.07 mol) in 100 mL of CH_2Cl_2 was added dropwise over 45 min to a solution of 1-(chloroacetyl)-4-(4-nitrophenyl)piperazine (10 g, 0.035 mol, prepared from chloroacetyl chloride and 1-(4-nitrophenyl)piperazine in a procedure similar to that described in 7) in 400 mL of CH_2Cl_2 at 0 °C. After stirring for 3 h, the reaction mixture was washed with aqueous HCl (pH 3) (CAUTION! Excess HCN is present) until the washings were at pH 7 and then with H_2O . The organic layer was separated, dried over Na_2SO_4 , filtered, and evaporated to give a yellow solid (9 g, 92%), which was used without further purification: ¹H NMR (CDCl_3) δ 3.48 (m, 2, CH_2N), 3.59 (m, 2, CH_2N), 3.70 (s, 2, CH_2), 3.75 (m, 2, CH_2N), 3.85 (m, 2, CH_2N), 6.86 (d, 2, Ar), 8.18 (d, 2, Ar).

1-[2-Cyano-3-[4-(*N,N*-diethylamino)phenyl]propenoyl]-4-(4-nitrophenyl)piperazine (1). In a procedure similar to that described in 10, 4-(*N,N*-diethylamino)benzaldehyde (1.77 g, 0.01 mol) and 4 (2.74 g, 0.01 mol) were reacted. The yellow product precipitated and was filtered, triturated with hot EtOH, and dried: yield 3.5 g (81%); mp 169–170 °C; ¹H NMR (CDCl_3) δ 1.23 (t, 3, CH_3), 3.45 (q, 2, CH_2), 3.54 (t, 4, CH_2N), 3.89 (t, 4, CH_2N), 6.68 (d, 2, Ar), 6.85 (d, 2, Ar), 7.79 (s, 1, =CH), 7.87 (d, 2, Ar), 8.16 (d, 2, Ar). Anal. Calcd for $\text{C}_{24}\text{H}_{25}\text{N}_5\text{O}_3$: C, 66.81; H, 5.84; N, 16.23. Found: C, 66.67; H, 6.33; N, 16.30.

2-Cyano-3-[4-(*N,N*-dimethylamino)phenyl]propenoic Acid (5). Cyanoacetic acid (4.7 g, 0.055 mol) and 4-(*N,N*-dimethylamino)benzaldehyde (7.45 g, 0.05 mol) were heated in EtOH overnight at reflux with a catalytic amount of piperidine. A dark yellow precipitate formed during reflux and was collected, dried, and used without further purification: yield 10 g (93%); ¹H NMR (CD_3OD) δ 3.1 (s, 6, CH_3N), 6.8 (d, 2, ArH), 7.9 (d, 2, ArH), 8.05 (s, 1, vinyl H).

1-[2-Cyano-3-[4-(*N,N*-dimethylamino)phenyl]propenoyl]-4-phenylpiperazine (3). Compound 5 (1 g, 0.005 mol) was dissolved in DMF (50 mL). CDI (0.81 g, 0.005 mol) was added and the solution stirred for 30 min at room temperature. *N*-Phenylpiperazine (0.81 g, 0.005 mol) was added dropwise to the orange solution and stirring continued for 1 h. The DMF solution was diluted with Et_2O (100 mL), and H_2O (100 mL) was added. The layers were separated, and the Et_2O layer was washed with aqueous HCl (pH 2, 100 mL), followed by aqueous NaHCO_3 (pH 8, 100 mL). A yellow precipitate formed in the Et_2O layer and was collected and washed with Et_2O : yield 1.5 g (83%); mp 133–5 °C; ¹H NMR (CDCl_3) δ 2.97 (s, 6, CH_3N), 3.15 (t, 4, CH_2), 3.75 (t, 4, CH_2), 6.57 (d, 2, ArH), 6.8 (m, 3, ArH), 7.2 (t, 2, ArH), 7.65 (s, 1, vinyl H), 7.8 (d, 2, ArH); MS m/e (rel intens): 360 (60, M^+), 239 (81), 199 (92), 132 (100), 56 (75). Anal. Calcd for $\text{C}_{22}\text{H}_{24}\text{N}_4\text{O}$: C, 73.31; H, 6.71; N, 15.54. Found: C, 73.03; H, 6.71; N, 15.40.

X-ray Crystal Structure. The crystallographic analysis was performed by Molecular Structure Corp., College Station, TX. A sample of 3 was recrystallized from MeOH. A $0.200 \times 0.050 \times 0.350$ mm yellow plate was used. Cell dimensions (monoclinic system, space group $P2_1$) are $a = 7.351$, $b = 6.044$, and $c = 21.418$ Å, $\beta = 94.59^\circ$, density = 1.262 and $Z = 2$. The data were collected at -140 °C, using a maximum 2θ of 120.2° and were refined to R of 0.057 and R_w of 0.068. The full crystallographic report, including positional and thermal parameters, is

available as supplementary material.

***N,N*-Dimethyl-2-cyano-3-[4-(*N,N*-dimethylamino)phenyl]propenamide (6).** In a procedure similar to that described for the preparation of compound 5, 4-(*N,N*-dimethylamino)benzaldehyde (3.7 g, 0.025 mol) and *N,N*-dimethylcyanoacetamide²¹ (2.8 g, 0.025 mol) were reacted, and a yellow solid was collected. Excess aldehyde was separated from the product by column chromatography on silica gel (50 g) eluting with hexane/ethyl acetate mixtures: UV-vis (acetone) 390 nm; ¹H NMR (CDCl_3) δ 3.1 (s, 6, CH_3N), 6.7 (d, 2, ArH), 7.7 (s, 1, vinyl H), 7.8 (d, 2, ArH). Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{N}_4\text{O}_2$: C, 64.5; H, 6.86; N, 20.06. Found: C, 65.17; H, 5.77; N, 19.73 (hemihydrate).

4-(4-Acetyl)piperazinyl-1-nitrobenzene (7). Acetic anhydride (2 g, 0.02 mol) in 50 mL of CH_2Cl_2 was added dropwise over 30 min to a stirred solution of 1-(4-nitrophenyl)piperazine (4.1 g, 0.02 mol) and triethylamine (2 g, 0.02 mol) in 200 mL of CH_2Cl_2 at 0 °C. After stirring for 2 h, the solution was washed twice with H_2O , and the organic layer was dried over Na_2SO_4 , filtered, and evaporated to give 4.5 g (90%) of yellow solid: mp 149–150 °C; ¹H NMR (CDCl_3) δ 2.17 (s, 3, CH_3), 3.47 (m, 4, CH_2N), 4.7 (t, 2, CH_2N), 4.85 (t, 2, CH_2N), 6.84 (d, 2, Ar), 8.16 (d, 2, Ar). Anal. Calcd for $\text{C}_{12}\text{H}_{15}\text{N}_3\text{O}_3$: C, 57.82; H, 6.06; N, 16.85. Found: C, 57.65; H, 5.99; N, 16.7.

4-[4-(Trifluoroacetyl)piperazinyl]benzaldehyde (9). A solution of *N*-phenyl-*N'*-trifluoroacetyl piperazine (prepared from *N*-phenylpiperazine and trifluoroacetic anhydride in $\text{NEt}_3/\text{CH}_2\text{Cl}_2$, 6.5 g, 0.025 mol) in 15 mL of 1,2-dichloroethane (DCE) was added to DMF/ POCl_3 (0.027 mol) in 15 mL of DCE as described previously.⁹ The mixture was heated at reflux for 1 h, with vigorous evolution of HCl. After cooling, the solution was diluted with additional DCE, washed cautiously with aqueous NaHCO_3 , dried, and used without further purification: mp 73–5 °C; ¹H NMR (CDCl_3) δ 3.5 (m, 4, CH_2), 3.8 (m, 4, CH_2), 6.9 (d, 2, ArH), 7.8 (d, 2, ArH), 9.8 (s, 1, CHO).

2-Cyano-3-[4-(4-(trifluoroacetyl)piperazinyl]phenyl]propenoic Acid (10). Compound 9 (1 g, 0.0035 mol) and cyanoacetic acid¹⁰ (0.3 g, 0.0035 mol) were dissolved in EtOH (100 mL). Piperidine (10 drops) was added and the solution refluxed overnight. After cooling, the solution was poured into ice water (50 mL). The yellow precipitate was collected and used without further purification: yield 0.8 g, (67%); mp 225–227 °C; ¹H NMR δ 3.57 (m, 4, CH_2), 3.7 (m, 4, CH_2), 7.15 (d, 2, ArH), 7.95 (d, 2, ArH), 8.08 (s, 1, vinyl H).

2-Cyano-3-(4-piperazinylphenyl)propenoic Acid (11). Compound 10 (1.2 g, 0.0034 mol) was added to H_2O (75 mL) and the solution vigorously stirred. Tetrabutylammonium hydroxide (3.3 g (55%), 0.007 mol) was added dropwise. The solid dissolved, and the solution was stirred at room temperature overnight. HI (~0.9 g (47%), 0.0034 mol) was added to lower the pH to 6.5. The heterogeneous aqueous layer was washed twice with CH_2Cl_2 (100 mL) and filtered to collect the yellow solid: yield 0.6 g (70%); mp 240 °C dec; ¹H NMR ($\text{Me}_2\text{SO}-d_6$) δ 2.4 (s, 1, NH), 3.02 (m, 4, CH_2), 3.43 (m, 4, CH_2), 6.96 (d, 2, ArH), 7.78 (d, 2, ArH), 7.8 (s, 1, vinyl H). Anal. Calcd for $\text{C}_{14}\text{H}_{15}\text{N}_3\text{O}_2 \cdot 0.5\text{H}_2\text{O}$: C, 63.14; H, 6.06; N, 15.78. Found: C, 63.17; H, 6.28; N, 15.70.

Poly[1-[2-cyano-3-(4-piperazinyl)phenyl]propenoic acid] (2). Dried 11 (0.2 g, 0.8 mmol) and CDI (0.5 g, 0.9 mmol) were added to DMF and stirred at 90 °C for 3 h. Upon heating, 11 dissolved and the solution turned orange. Stirring was continued at room temperature overnight. The oligomer was precipitated by adding the DMF solution dropwise to 10% CH_2Cl_2 /petroleum ether and collected by filtration (60 mg); UV-vis (Me_2SO) 400 nm.

Acknowledgment. We thank F. M. Houlihan, F. S. Bates, and C. W. Dirk for helpful discussions. We also thank A. M. Majsce for obtaining mass spectra and G. E. Johnson, S. Mumby, and K. D. Singer for valuable advice pertaining to dielectric measurements.

Supplementary Material Available: X-ray crystal structure report for 3, including data collection, data reduction, and structure solution and refinement, and tables of positional and thermal parameters, experimental details, general temperature factor expressions, torsional angles, intermolecular contacts, least-squares planes, and intensity data (17 pages); tables of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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