Table I. ^{13}C NMR Spectra of Lithium Cyanocuprates

cuprates[a]	solvent[b]	temp, °C	C1[c]	C2	C3	C4	CN
$PhCu(^{13}CN)Li$	THF-d_8	−78	166.05, s	140.94	126.08	123.87	148.50
	THF-d_8/HMPA	−78	168.40, d (J = 24.2 Hz)	141.22	125.80	123.18	145.41
	THF-d_8/HMPA/12-C-4	−78	168.38, d (J = 24.2 Hz)	141.21	125.80	123.19	145.43
	THF-d_8	−100	165.97, d (J = 12.7 Hz)	140.92	126.10	123.90	148.33
	THF-d_8/HMPA	−100	168.33, d (J = 23.7 Hz)	141.19	125.83	123.23	145.38
	THF-d_8	−110	165.93, d (J = 23.3 Hz)	140.91	126.18	123.93	148.25
	ether-d_{10}	−78	166.03 (br s)	140.88	125.87	123.61	149.70
	ether-d_{10}/HMPA	−78	168.70, d (J = 24.2 Hz)	141.18	125.60	122.90	145.60
	ether-d_{10}/HMPA/12-C-4	−78	168.66, d (J = 23.7 Hz)	141.17	125.60	122.89	145.61
	ether-d_{10}	−100	165.99, d (J = 24.2 Hz)	140.82	125.85	123.57	149.42
$CH_3CH_2Cu(^{13}CN)Li$	THF-d_8	−78	1.64, d (J = 21.6 Hz)	15.54			149.11
	THF-d_8/HMPA/12-C-4	−78	1.92, d (J = 22.0 Hz)	16.05			146.47
	THF-d_8	−100	1.74, d (J = 22.0 Hz)	15.65			148.96
	ether-d_{10}	−78	1.85, s	15.32			150.86
	ether-d_{10}/HMPA	−78	2.04, d (J = 22.0 Hz)	15.92			146.76
	ether-d_{10}/HMPA/12-C-4	−78	2.05, d (J = 21.6 Hz)	15.93			146.76
	ether-d_{10}	−100	1.89, d (J = 20.8 Hz)	15.47			150.10
	ether-d_{10}/HMPA	−100	2.17, d (J = 21.6 Hz)	16.04			146.69
	ether-d_{10}/HMPA/12-C-4	−100	2.17, d (J = 21.6 Hz)	16.03			146.67
$^{13}CH_3Cu(^{13}CN)Li$	THF-d_8	−78	−12.85, s				149.34
	THF-d_8/HMPA	−78	−12.36, d (J = 22.0 Hz)				146.48, d
	THF-d_8/HMPA/12-C-4	−78	−12.42, d (J = 21.6 Hz)				146.56, d
	THF-d_8	−100	−12.60 (br s)				149.13
	THF-d_8/HMPA	−100	−12.04, d (J = 21.6 Hz)				146.36, d
	THF-d_8	−110	−12.46, d (J = 20.8 Hz)				148.97, d
$CH_3Cu(^{13}CN)Li$	ether-d_{10}	−78	−12.58, s				151.01
	ether-d_{10}/HMPA	−78	−11.97, d (J = 21.6 Hz)				146.76
	ether-d_{10}/HMPA/12-C-4	−78	−11.93, d (J = 21.6 Hz)				146.77
	ether-d_{10}	−100	−12.25 (br s)				150.20
	ether-d_{10}	−110	−12.10, d (J = 12.3 Hz)				149.95
	ether-d_{10}	−120	−11.93, d (J = 21.6 Hz)				149.78

[a] In the cases of EtCu(CN)Li and of MeCu(CN)Li in THF-d_8, the Li is ^{6}Li. [b] To 3 mL of THF-d_8 or ether-d_{10} were added 312 μL of HMPA and 100 μL of 12-C-4. [c] Chemical shifts are referenced to the δ 67.391 line in the spectrum of THF-d_8 and the 14.707 ppm line in the spectrum of ether-d_{10}. J values are ±0.04 Hz. The spectra were obtained on a Bruker AM360 NMR spectrometer.

as $R_2CuLi{\cdot}LiCN$. The lack of coupling between ^{13}CN and C1 in $R_2CuLi{\cdot}Li^{13}CN$ also mitigates against the higher order formulation, although exchange may be responsible for the lack of coupling in these cases.

Dimethylmercury is a linear molecule that has a value of ^2J = 22.4 Hz.[10] The relatively large magnitude of ^2J for RCu(CN)Li suggests a linear structure as well. The two-bond ^{13}C–^{13}C couplings between cis carbonyls (bond angle 90°) in a series of pentacarbonyl metal–carbene complexes fall in the range 2.7–5.4 Hz.[11] The magnitude of ^2J is dependent upon the hybridization of the intervening orbitals;[2] however, in our case this effect is small, as can be seen by comparing our values for phenyl- and alkylcuprates.

The addition of 12-crown-4 to cuprates has been shown to yield monomeric species,[12] and the addition of HMPA to PhLi aggregates has been shown to yield monomers as well.[13] Consequently, we presume that RCu(CN)Li is monomeric in the presence of HMPA and 12-crown-4. When RCu(CN)Li is cooled to a low enough temperature, it is possible to obtain ^2J equal to the value in the presence of HMPA and 12-crown-4, where coupling is observed at −78 °C in every case. This observation does not necessarily imply monomers at those temperatures, since the RCuCN units in a dimer might be linear.[14] Nevertheless, it has been shown that Li reagents afford smaller aggregates as the temperature is lowered in coordinating solvents.[4] Under those conditions where coupling in $RCu(^{13}CN)Li$ is not observed, an exchange process mediated by Li appears to be involved. This exchange may involve the formation of dimers.

Registry No. $PhCu(^{13}CN)Li$, 133930-77-5; $CH_3CH_2Cu(^{13}CN)Li$, 133930-78-6; $^{13}CH_3Cu(^{13}CN)Li$, 133930-79-7; $CH_3Cu(^{13}CN)Li$, 133930-80-0.

Supplementary Material Available: NMR spectra of $[CH_3CH_2Cu^{13}CN]^{-}{}^6Li^+$ and $[CH_3CH_2CuCN]^{-}{}^6Li^+$ (1 page). Ordering information is given on any current masthead page.

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Design and Synthesis of New Ferroelectric Liquid Crystals. 14.[1] An Approach to the Stereocontrolled Synthesis of Polar Organic Thin Films for Nonlinear Optical Applications

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Optical quality thin film materials possessing large $\chi^{(2)}$ (second-order nonlinear optical (NLO) susceptibility) are of clear

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Table I. Values of the Ferroelectric Polarization, SHG Efficiency, and $\chi^{(2)}$ (d_{eff} and d Coefficients) for Representative FLCs and for the FLC Phase of **1**[c]

entry number	compound	**P** (nC/cm^2)	SHG arb units[a]	d_{eff} (pm/V)	d coefficients (pm/V)
1	DOBAMBC[8c]	−3	1	0.0008	
2	ZLI 3654[8d-f]	−29	40	0.005	
3	SCE 9[8g]	+33.6	160	0.01	$d_{23} = 0.073$ $d_{22} = 0.027$ $d_{21} = 0.0026$ $d_{25} = 0.0009$
4	**1**[13]	−420[b]	8×10^4	0.23	$d_{23} = 0.63 \pm 0.03$ $d_{22} = 0.6 \pm 0.3$ $d_{21} = 0.08 \pm 0.02$ $d_{25} = 0.16 \pm 0.05$
5	KH_2PO_4 (KDP)[14]				$d_{36} = 0.39$
6	$KTiOPO_4$ (KTP)[15]				$d_{31} = 5.9$

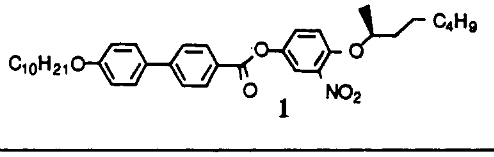
[a] Intensity of the second harmonic light at the top of the type 1 eeo angle phase-matched peak. [b] The SHG measurements with compound **1** were performed at 60 °C, where $\mathbf{P} \cong -420$ nC/cm^2. [c] Values for some common inorganic NLO crystals are included for comparison.

potential applicability in photonics. The problem of creation of such materials with organic molecules, a potentially attractive approach,[2] involves two fundamental considerations: (1) design and synthesis of organic functional arrays (molecules) possessing appropriate molecular second-order susceptibility β and (2) combination of the NLO molecules in a *material* on the order of 10 000-Å thick and perhaps centimeters on a side with the correct stereochemistry. With regard to the latter, controlled *polar orientation* of the NLO active groupings is of clear utility for design of $\chi^{(2)}$ materials. While considerable progress in the molecule problem has resulted from techniques of classical stereo- and regiocontrolled organic synthesis in combination with relatively simple theoretical arguments, achieving polar stereocontrol in the *material* is still difficult and under intensive study worldwide.[3-7] We report herein successful application of the Boulder Model for the molecular origins of the spontaneous polar order in ferroelectric liquid crystals (FLCs)[1] to the synthesis of organic films with good stereocontrol in the orientation of the *o*-nitroalkoxy functional array and relatively large, stable $\chi^{(2)}$.

FLCs are true liquids which nevertheless possess spontaneous polar order, a property required by the symmetry of the system. FLCs thus typically possess a measurable macroscopic electric dipole moment, the ferroelectric polarization **P**, deriving from net polar orientation of molecular dipoles in the film. Shortly after the experimental demonstration of polar order in FLCs, several groups began investigation of the nature of $\chi^{(2)}$ of FLC phases, knowing that the same polar order required for nonzero **P** is also sufficient, though not necessary, for nonzero $\chi^{(2)}$ in the simple electronic dipolar model.[8,9]

Unfortunately, the measured values of the ultrafast $\chi^{(2)}$ in several FLCs, as evidenced by second harmonic generation (SHG) from 1064-nm light, showed that these FLCs possess very small $\chi^{(2)}$. Table I gives relevant experimental results on representative FLCs. The examples given in entries 1, 2, and 3 illustrate the problem: Given the values for typical inorganic crystals in use today (entries 5 and 6), the values of d_{eff} obtained for the classic FLC material DOBAMBC and for the commercial mixtures ZLI 3654 and SCE 9 are so small as to suggest FLCs would be useless in NLO applications.

On the basis of the Boulder Model for the polar order in FLCs we felt that the low $\chi^{(2)}$ values observed for typical FLCs was due to a combination of two factors: (1) poor stereocontrol and (2) orientation of functional arrays with small β along the polar axis. With a design approach detailed in recent publications,[1,10] we felt that the (*o*-nitroalkoxy)phenyl biphenylcarboxylate (**1**) would exhibit good polar orientation of the *o*-nitroalkoxy unit, which also should possess reasonable β (about 0.15 times *p*-nitroaniline) based upon standard arguments.[11]



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(10) Experiments verifying the validity of the approach to design of compounds of type **1** is given in ref 1d (the proceedings of the 2nd International Ferroelectric Liquid Crystal Conference, Göteborg, Sweden, June 29–July 1, 1989). Pioneering work with a class of FLCs similar to **1** (but where the nitro grouping is replaced by various halogens and by cyano) is presented: Furukawa, K.; Terashima, K.; Mitsuyoshi, I.; Saitoh, S.; Miyazawa, K.; Inukai, T. *Ferroelectrics* **1988**, *85*, 451–459. It is interesting to note that compound **1** possesses the largest polarization of any material in this class.

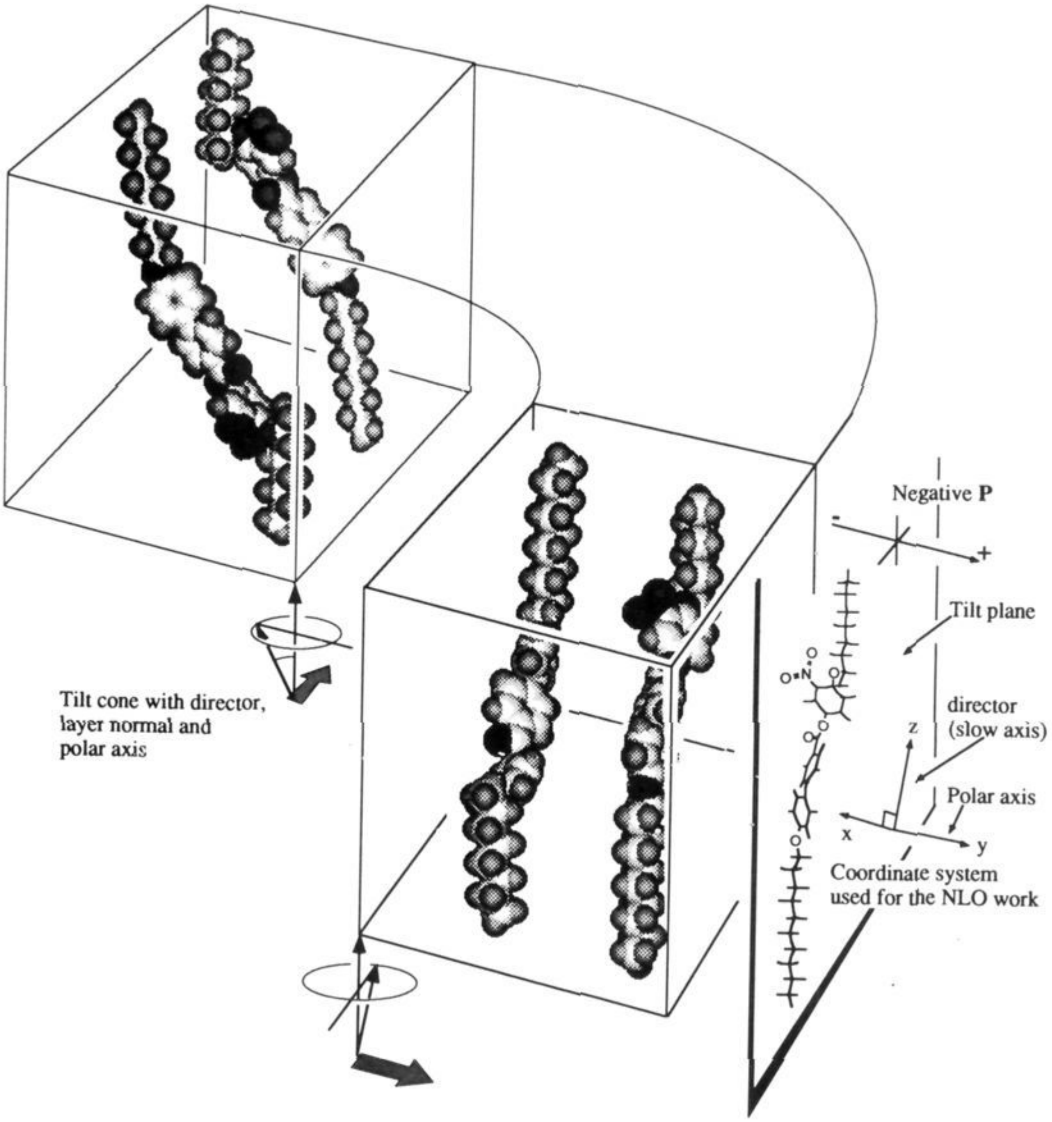

Figure 1. Orthogonal views illustrating the proposed structure of FLC films of **1**.

Indeed, experimental measurements of the macroscopic dipole density **P** by the polarization reversal current method provides good evidence that the nitroalkoxy unit is oriented along the polar axis of FLC films of **1** with relatively good stereocontrol.[1a,b] Thus, at room temperature the measured polarization of **1** is −560 nC/cm^2 ≅ −2.1 D/molecule. Assuming that the molecular dipole moment of the nitroalkoxy unit is perfectly aligned along **P** and estimating this to be about 5 D (for (*o*-nitromethoxy)benzene, $\mu = 4.8$ D[12]), fully 40% of the important molecular functional array is oriented along **P** in the *liquid* phase.

Our interpretation of this result is illustrated in Figure 1, which shows the effective "unit cell" of the FLC phase, with two molecules of **1** related by a 2-fold axis. In the figure the molecules are oriented with respect to conformation (a Tripos force field minimum is shown in the drawing) and rotational orientation relative to the tilt plane according to the Boulder Model. It should be stressed that the conformer shown actually represents a large family of conformations, keeping in mind that the phase in question is a liquid. Note that the nitroalkoxy unit is well-oriented along **P** according to this proposed liquid crystal structure, affording a film with good stereocontrol for $\chi^{(2)}$.

Preliminary experiments with parallel-aligned samples of **1** indicated it possessed the largest $\chi^{(2)}$ of any FLC measured to date.[1a,b] Indeed, as shown in Table I, the *d* coefficients for homeotropic films of **1** are large compared to other FLCs, and the observed values seem quite consistent with the interpretation of the structure of the phase as inferred from the polarization measurement and shown in the figure.

It should be noted that poled polymer films exhibiting susceptibilities about 2 orders of magnitude larger than that for films of **1** have been reported.[5e] In these films, however, the NLO active units possess much larger β and far red-shifted resonant absorptions relative to **1** (ref 5e reports a d_{33} of 40 pm/V for a polyphosphazine functionalized with the disperse red **1** NLO-active moiety). The degree of stereocontrol (percentage of dipoles aligned along **P**) in the FLC is actually considerably greater than can be achieved by poling. Also, in the FLC (and also in FLC polymer glasses)[16] the polar structure is a thermodynamic global minimum,

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[11] While we have not found a report giving β for *o*-nitroanisole, the largest component should be about 5 × 10^{-30} esu based upon the following experimental $|\vec{\beta}|$ values (all in the same units): *p*-nitroaniline ≅ 35; *o*-nitroaniline ≅ 10; *p*-nitroanisole ≅ 15. For comparison, the $|\vec{\beta}|$ of fluorobenzene is reported to be 0.4, while that of urea is 2.3. The data are from ref 2 and the following references: (a) Dulcic, A.; Sauteret, C. *J. Chem. Phys.* **1978**, *69*, 3453–3457. (b) Dirk, C. W.; Twieg, R. J.; Wagnière, G. *J. Am. Chem. Soc.* **1986**, *108*, 5387–5395. (c) Li, D.; Marks, T. J.; Ratner, M. A. *Chem. Phys. Lett.* **1986**, *131*, 370–375.

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in sharp contrast to the kinetically stabilized but thermodynamically unstable polar structure obtained in poled polymers. Many clear directions for tuning of the NLO properties of FLC films for various applications are suggested by the work presented here and are under active investigation in our labs.

In conclusion, we provide evidence with second-order NLO measurements of the basic correctness of the model of the structure of films of compound **1** in the FLC phase summarized in Figure 1. These results suggest that it is possible to achieve stereocontrolled synthesis of organic thin films of interest for second-order NLO applications in a directed manner with the FLC self-assembly in combination with the Boulder Model. The generality of the approach is being explored.

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Aromatic Architecture. Use of the *N*-Methylamide Structure as a Molecular Splint

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The stereochemical alteration caused by N-methylation of an aromatic amide structure is an efficient means of changing the biological activity of a molecule, as we have found during the drug design of synthetic retinoids[1] and synthetic cytokinins.[2] *N*-Methylbenzanilide (**1**) exists predominantly in a cis amide conformation in solution and in the crystal, while benzanilide (**2**) exists in a trans conformation.[3] Though the cis conformation is superficially less favorable, this seems a rather common phenomenon intrinsic to aromatic *N*-methylamides. The cause of this real stabilization of the cis structure is unclear and is under study. The cis preference can be used for the fixation of a molecule in a shape that seems less favorable from simple stereochemical considerations. In this paper, we present some examples of molecular construction by using an *N*-methylamide structure as a splint or a scantling in a molecule.

The crystal structure of *N*,*N*′-dimethylterephthalic dianilide (**3**) is shown in Figure 1. The stereochemistry of each *N*-methylbenzanilide moiety is very similar to the structure of **1**. The NMR spectrum[4] of **3** also indicates that the conformation is close to the crystal structure because the signals of the aromatic protons of the terminal rings are as expected from the NMR spectrum of **1**,[3] suggesting that anti stereochemistry is predominant in solution too. The crystal structure of *N*,*N*′-dimethylisophthalic dianilide (**4**) is shown in Figure 2. The crystal cis stereochemistry of the two amide bonds is as expected. The syn stereochemistry of the two terminal moieties is rather unexpected. The solution stereochemistry is also similar to the crystalline structure, because the two terminal protons of the anilide rings are shielded to a greater extent than the corresponding protons of **1**.

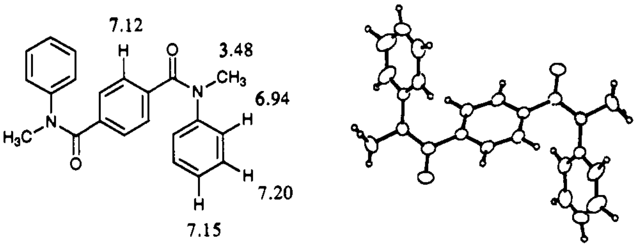

Figure 1. Structure and an ORTEP view of **3**.

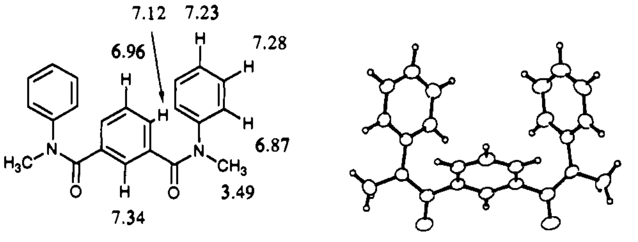

Figure 2. Structure and an ORTEP view of **4**.

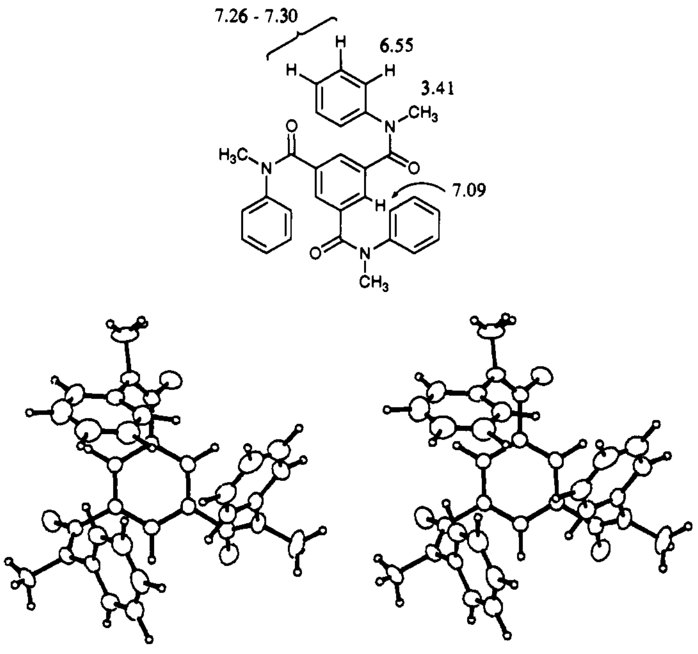

Figure 3. Structure and an ORTEP stereoview of **5**.

A more interesting molecular structure was found for the trianilide of trimesic acid. The crystal structure of trimethyl derivative **5** is shown in Figure 3. All three phenylcarbamoyl groups exist in a cis conformation, and surprisingly, all of them are in syn conformation. Since the steric crowdedness of the conformation is evident, the stabilization of the all-syn structure is definitely due to the bonding interactions of the three benzene rings (distorted T-shaped interaction).[5] The particularly high

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(4) NMR spectra were analyzed in $CDCl_3$. Chemical shifts (at −60 °C) for compounds **3**–**5** and **7** are shown in the figures. The dynamic aspects will be discussed elsewhere.

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