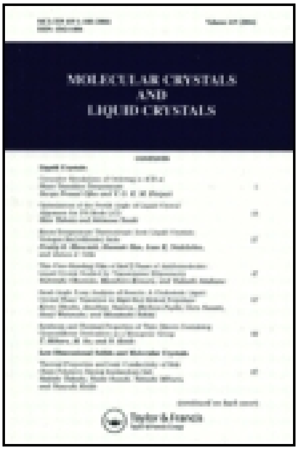


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl18

An Approach to the Design of Ferroelectric Liquid Crystals with Large Second Order Electronic Nonlinear Optical Susceptibility

David M. Walba [a], M. Blanca Ros [a], Noel A. Clark [b], Renfan Shao [b], Kristina M. Johnson [c], Michael G. Robinson [c], J. Y. Liu [c] & David Doroski [c]

[a] Department of Chemistry and Biochemistry and Optoelectronic Computing Systems Center, University of Colorado, Boulder, CO, 80309-0215

[b] Department of Physics and Optoelectronic Computing Systems Center, University of Colorado, Boulder, CO, 80309-0390

[c] Department of Electrical and Computer Engineering and Optoelectronic Computing Systems Center, University of Colorado, Boulder, CO, 80309-0425

Version of record first published: 24 Sep 2006.

To cite this article: David M. Walba , M. Blanca Ros , Noel A. Clark , Renfan Shao , Kristina M. Johnson , Michael G. Robinson , J. Y. Liu & David Doroski (1991): An Approach to the Design of Ferroelectric Liquid Crystals with Large Second Order Electronic Nonlinear Optical Susceptibility, Molecular Crystals and Liquid Crystals, 198:1, 51-60

To link to this article: http://dx.doi.org/10.1080/00268949108033382

Mol. Cryst. Liq. Cryst., 1991, Vol. 198, pp. 51–60
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

An Approach to the Design of Ferroelectric Liquid Crystals with Large Second Order Electronic Nonlinear Optical Susceptibility

DAVID M. WALBA* and M. BLANCA ROS

Department of Chemistry and Biochemistry and Optoelectronic Computing Systems Center, University of Colorado, Boulder, CO 80309-0215

and

NOEL A. CLARK and RENFAN SHAO

Department of Physics and Optoelectronic Computing Systems Center, University of Colorado, Boulder, CO 80309-0390

and

KRISTINA M. JOHNSON, MICHAEL G. ROBINSON, J. Y. LIU and DAVID DOROSKI

Department of Electrical and Computer Engineering and Optoelectronic Computing Systems Center, University of Colorado, Boulder, CO 80309-0425

(Received August 20, 1990)

Ferroelectric liquid crystal thin films in the Clark-Lagerwall surface-stabilized geometry exhibit well known spontaneous polar orientation of functional groups. The symmetry of the system thus allows the existence of bulk electronic second order nonlinear hyperpolarizability $\chi^{(2)}$ within the context of the simple dipolar model. For all FLC materials examined to date, however, the magnitude of $\chi^{(2)}$ is small, presumably since the particular functional group arrays oriented along the polar axis possess small molecular hyperpolarizability β.

Using the Boulder Model for the molecular origins of the polar order occurring in FLC films, it is possible to design materials with functionalized aromatic rings oriented along the polar axis of the film. Since such functional arrays may show respectable values of β, it should be possible to obtain FLC films (both low molecular weight and polymeric) with useful magnitude of $\chi^{(2)}$ using this approach. Results of initial experiments aimed at design of FLC materials with large $\chi^{(2)}$ will be described.

INTRODUCTION AND BACKGROUND

It is well recognized that materials possessing fast and large nonlinear optical (NLO) susceptibilities are of great potential utility in the emerging photonics industry.[1] Indeed, materials possessing second order nonlinearity $\chi^{(2)}$ are already used in frequency mixing (e.g., crystals for second harmonic generation) and optical switching (e.g., the AT&T $LiNbO_3$ directional couplers) applications. In addition, $\chi^{(2)}$ materials which can be processed into thin films on a variety of substrates show great promise as components of integrated optical devices.

In order to realize the potential of $\chi^{(2)}$ materials, however, improvements in the magnitude of the second order nonlinearity and processibility are necessary. In this regard organic materials are of great interest. Thus, it is well known that organic molecules may possess relatively large molecular second order hyperpolarizability β, and considerable research activity is currently focussed upon discovering the optimum functional group arrays for achieving very large β. To translate molecular NLO susceptibility into the bulk $\chi^{(2)}$ necessary for optical processing, however, the molecular functional arrays must be assembled into a *material* (simply a collection of atoms usually about 1 μm = 10,000 Å thick and perhaps 1 cm on a side) with a certain specific stereochemistry and high optical clarity. In our view this problem is really one of stereocontrolled synthesis, and stands at an exciting current frontier at the interface between chemistry and materials science.

In fact, the required $\chi^{(2)}$ material could be a single huge molecule with proper stereochemistry.[2] Other approaches under active investigation include the use of organic crystals,[3] electrically poled polymer glasses,[4] Langmuir-Blodgett films (LB films)[5] and self-assembling multilayers (SAMs).[6] All of these are highly interesting, but each is to some extent flawed by technical or fundamental difficulties. Thus, though great strides are being made in the field, organic single crystals are difficult to design with precision, and are difficult to process into optical quality films, as are LB films and SAMs. Finally, poled polymers must rely upon kinetic stabilization of appropriate stereochemistry in the polymer glass to remain NLO active, and the stereocontrol achieved in the poling process under the best circumstances is poor.

While the rapid pace of research exploring all aspects of these approaches suggests that useful materials will derive therefrom, we feel that the ferroelectric liquid crystal (FLC) self assembly provides a particularly elegant and potentially very useful solution to the problem of creation of $\chi^{(2)}$ thin films. A description of recent progress in a nascent project directed towards realizing this potential follows.[7]

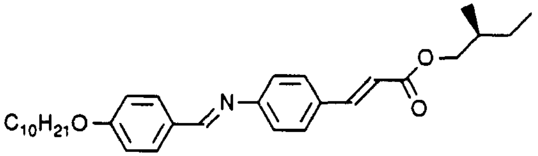
$\chi^{(2)}$ FLCs—Results with Commercial FLC Materials

It seems to be well known by all in the field that in order to possess non-zero $\chi^{(2)}$ within the electronic dipolar model (and probably in general for large $\chi^{(2)}$) noncentrosymmetric (acentric) symmetry is required. In addition, orientation of functional arrays possessing large β along the polar axis of a *polar material* provides a promising approach for design of materials with large $\chi^{(2)}$.

At this point it seems useful to digress slightly in order to discuss how molecular chirality forces symmetry-lowering in condensed matter in the context of symmetry-allowed $\chi^{(2)}$. Thus, the necessary and sufficient symmetry condition for non-zero $\chi^{(2)}$ in the electronic dipolar model is acentricity.[1] Any material composed of nonracemic molecules must be acentric. Even an isotropic chiral liquid is acentric, and indeed possesses non-zero antisymmetric elements of the $\chi^{(2)}$ tensor, as first pointed out by Giordmaine.[8] While these elements do not afford second harmonic generation (SHG; a standard probe of electronic second order susceptibility), sum and difference frequency generation *has been demonstrated* in chiral isotropic liquids.[9]

In order to achieve *large* $\chi^{(2)}$, however, it seems generally true that molecular βs should be aligned along a *polar axis*. All materials with polar symmetry are acentric, but not all acentric materials are polar (e.g., the chiral isotropic liquid).[10] The key point is the following: In FLC phases, molecular chirality does not simply force acentricity (as it would for an isotropic liquid), but actually forces *polar order*.

Not surprisingly, the spontaneous polar order occurring in FLCs prompted NLO experiments in FLC films as early as 1981.[11] Perhaps more surprisingly at first, the susceptibilities observed for classic FLC materials such as DOBAMBC were extremely small, even though it seems that the magnitude of β along the director should be substantial. This early work underscores an interesting problem with FLCs for NLO. Specifically, while the polar axis in the FLC phase is normal to the director, the large component of β for FLC mesogenic molecules would typically be *along* the director. Thus, though the FLC phase seems to have the appropriate symmetry for large $\chi^{(2)}$, lack of *stereocontrol* (no polar order along the director, and small βs normal to the director) leads to small susceptibility.



DOBAMBC

Thus, prior to our work the commercial E. Merk mixture ZLI 3654 was shown by Taguchi, Ouchi, Takezoe and Fukuda to possess the largest known second order susceptibility for an FLC material.[12] The geometry of the experiment is given in Figure 1. A homeotropic cell is irradiated with the fundamental (1064 nm light from a Nd:YAG laser) polarized in the *xz* plane (extraordinary beam). Second harmonic light (532 nm) colinear with the fundamental, but polarized along *y* (ordinary beam), is generated. The cell is rotated about the polar axis, and the SHG intensity as a function of input angle is measured (type 1 eeo angle phase-matching). This allows an estimate of the magnitude of d_{eff}, a measure of a combination of the components of $\chi^{(2)}$, which for ZLI 3654 was very small: $|d_{\text{eff}}|$ ZLI 3654 $\cong 0.0025$ times $|d_{22}|$ $LiNbO_3$.

In order to more precisely calibrate the nonlinearity of FLCs relative to other materials, we have screened a number of commercial FLC mixtures from BDH, and found that the mixture SCE9 showed the largest nonlinearity. Using a combination of Maker fringe experiments in a homeotropic wedge cell and the above described type 1 eeo angle phase-matching in a 35 μm homeotropic cell with parallel bounding plates, the magnitude of all of the non-zero components of $\chi^{(2)}$ for SCE9 were determined, and are given below.[13]

$$\begin{aligned}\text{For SCE9:}\quad d_{y,zz} &= d_{23} = d_{34} = 0.073(2)\ \text{pm/V}\\ d_{y,yy} &= d_{22} = 0.027(1)\ \text{pm/V}\\ d_{y,xx} &= d_{21} = d_{16} = 0.0026(1)\ \text{pm/V}\\ d_{y,xz} &= d_{25} = d_{14} = d_{36} = 0.0009(1)\ \text{pm/V}\end{aligned}$$

In fact, SCE9 possesses the largest $\chi^{(2)}$ of any FLC reported to date, with d_{eff}

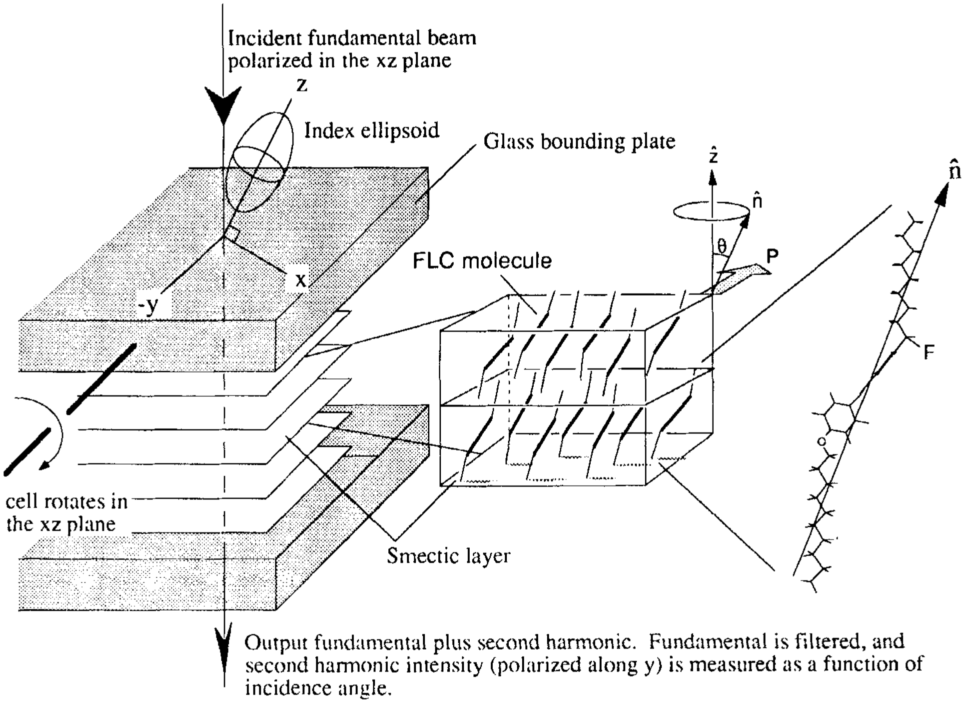


FIGURE 1 The geometry of a homeotropically-aligned FLC cell set up for type I eeo angle phase-matched SHG. Note that the spacing between the glass bounding plates (≅35 μm) and the smectic layer spacing (≅35 Å) are not to scale and that the index ellipsoid is exaggerated.

SCE9 ≅ 2 times d_{eff} ZLI 3654. Even so, the values for the FLC are quite small given that for $LiNbO_3$ d_{15} = 5 pm/V, and d_{22} = 3.2 pm/V. This is especially apparent since the promise of organic materials for NLO is that nonlinearities much *greater* than those of inorganic crystals should be possible. It is not, however, surprising, since the functional groups oriented along the polar axis in SCE9 are probably carbonyl, and perhaps cyanoalkyl groupings, which are expected to possess small β values (the composition of SCE9, **P** = 30 nC/cm^2, is not published).

First Generation FLCs Designed Specifically for $\chi^{(2)}$

The challenge, then, is to design FLC films where functional groups possessing *large* β are oriented along the polar axis. As is now well known, the prototype of such functional arrays consists of a donor grouping and an acceptor grouping oriented either ortho or para on an aromatic ring. Thus, in the FLC case, an important goal is to obtain orientation of *functionalized aromatic rings* along the polar axis of the FLC film.

While the symmetry argument proves that FLCs must possess polar order, symmetry alone does not suggest which functional groups are aligned along the polar axis, or how this orientation occurs on a molecular level. We have developed a simple stereochemical model for the molecular origins of the polar order occurring in FLCs,[14] and have demonstrated that considerable precision in the alignment of simple functional groups (e.g., C—F bonds and epoxide units) may be achieved by using the model to guide the design of FLC mesogens.[15]

Indeed, the FLC design group at Chisso have reported experimental results beautifully consistent with the model, and strongly suggesting that functionalized aromatic rings can be well oriented along the polar axis of FLC films.[16] More recently, we have also reported evidence for such orientation in an interesting *o*-alkoxypyridine and pyridine *N*-oxide FLC system.[17] In the materials synthesized in the latter systems, however, the oriented functional arrays are expected to possess relatively small β, leading to the expectation of small $\chi^{(2)}$ in the FLC films.

While expected to possess only moderate β, the second order molecular susceptibility of *o*-nitroanisole is certainly larger than that of simple unconjugated esters, halides, or nitriles. While we have not found a number for the β of *o*-nitroanisole, the largest component should be about 5×10^{-30} esu based upon the following experimental $|\beta|$ values (all in the same units): *p*-nitroaniline $\cong$ 35; *o*-nitroaniline $\cong$ 10; *p*-nitroanisole $\cong$ 15.[1,18] For comparison, the $|\beta|$ of fluorobenzene is reported to be 0.4, while that of urea is 2.3.

Based upon our own work and that of the Chisso group mentioned above, it seemed possible to achieve good orientation of the *o*-nitroalkoxy functional array along the polar axis in an FLC phase in such a way that a relatively large $\chi^{(2)}$ would result. To test this idea, the nitroaromatic FLC mesogens shown in Chart 1 were designed, prepared and characterized as the first FLC materials designed specifically for $\chi^{(2)}$.

While the Chisso group has reported similar *o*-halo and *o*-cyanoalkoxy-containing mesogens,[16] to our knowledge the *o*-nitro-substituted compounds have never been previously reported. The biphenylbenzoate core was chosen since this core, explored extensively by Gray and Goodby,[19] is well known to produce smectic C phases in abundance. These materials are typically considered uninteresting for FLCs to be utilized in the SSFLC device since the biphenylbenzoate core also confers high viscosity. For electronic NLO, however, orientational viscosity is not of primary importance since in $\chi^{(2)}$ applications no nuclear motions are necessary.

In terms of functional group orientation, the very straightforward rationale behind the structures shown in Chart 1 is illustrated in Figure 2. Thus, according to the model, for the *o*-nitro-1-methylheptyloxy compounds **1** and **3–5**, conformers of type **A**, **B**, and **C** should all fit the C* "lattice" equally well, but conformers **A** and **B** should be favored due to the larger *internal* steric strain present in conformer **C** relative to **A** and **B** (molecular mechanics calculations suggest that **A** is the gas phase global minimum).

In fact, the data given in Chart 1 support this model quite well. All of the *o*-nitroalkoxy compounds show large negative **P**. The *m*-nitro compound **2**, prepared as a control, also shows properties fully consistent with the model. Here, the polarization observed is similar to that of the unsubstituted 1-methyl-heptyloxy biphenylbenzoate (**P** $\cong -55$ nC/cm^2; $\theta \cong 27°$, **P**/sin$\theta = -121$ @ T—Tc $= -10$),[20] since no anisotropic orientation of the nitro grouping relative to the tilt plane should occur.

The observed properties of neat FLC **1** deserve special comment. Note that this

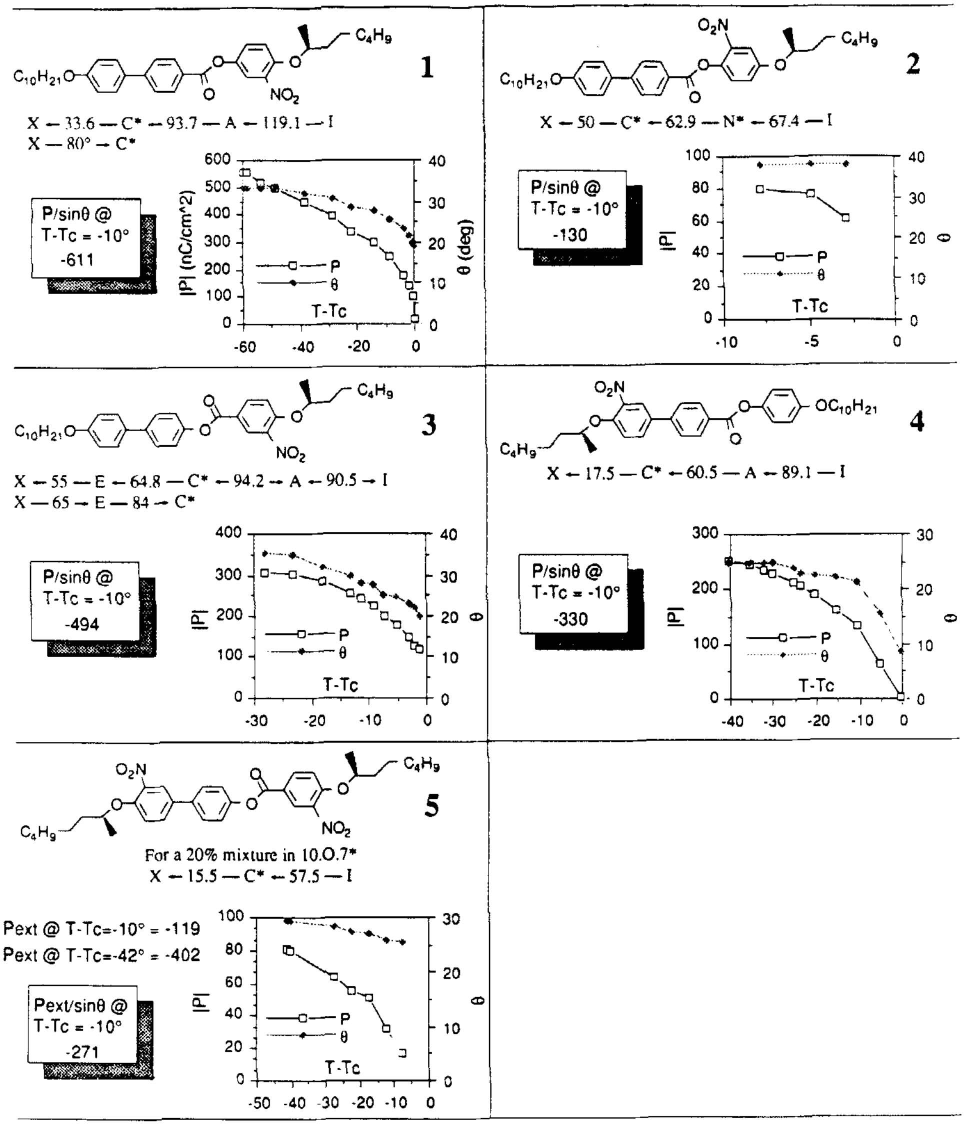


CHART 1 Structure, phase sequence, polarization and tilt angle data on the first generation FLCs designed for $\chi^{(2)}$.

compound possesses a very broad monotropic C* phase range, and before crystallization (at about 31°C) shows the highest polarization density, as measured by the polarization reversal current method[21] using a triangular drive wave, of any neat FLC material reported to date to our knowledge (-556 nC/cm^2 $\cong$ -2.1 D/molecule)! Interestingly, the value of the normalized polarization (**P**/sinθ) at T—Tc = -10°C is larger than that of any of the *o*-cyanoalkoxy FLC mesogens reported by the Chisso group.

According to the model, the polarization of an FLC is given by Equations 1 and

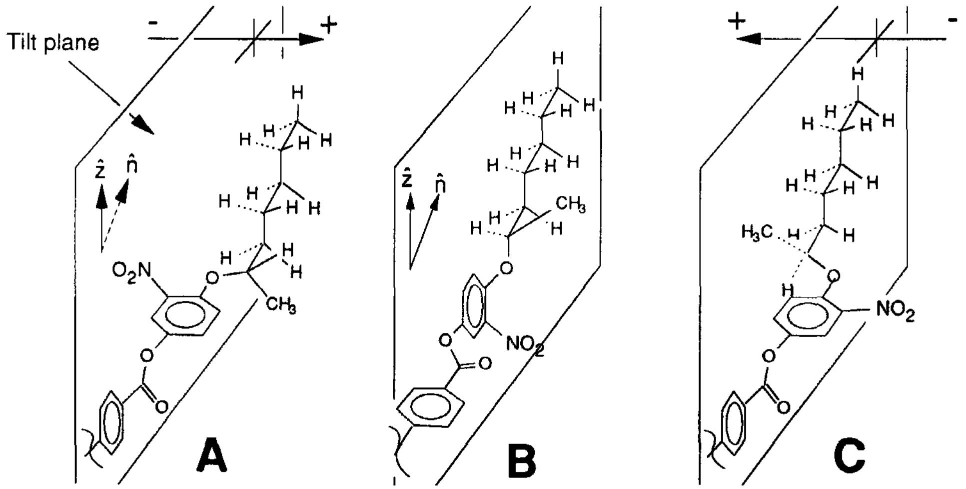


FIGURE 2 Important conformational and rotational orientations in the C* phase for *o*-nitroalkoxy compounds of type **1**.

2, where D_i is the number density of the *i*th conformation, $\mathbf{P}_i$ is the contribution to the polarization for the *i*th conformation, $\hat{\mu}_{\perp i}$ is the component of the molecular dipole moment oriented normal to the tilt plane for the *i*th conformation when the conformer is at the bottom of the rotational energy well, and ROF_i is a number between zero and one reflecting the degree of rotational ordering.[22] If one assumes *perfect* rotational orientation as indicated for conformer A in Figure 2, and $\hat{\mu}_{\perp}$ = 4.8D (the value for *o*-nitroanisole), then the expected polarization $\mathbf{P} = -4.8$ D/molecule. With an observed $\mathbf{P} = -2.1$ D/molecule, in the FLC phase at 31.2°C the *o*-nitroalkoxy unit must be quite well oriented along the polar axis of the phase as shown in Figure 2A.

$$\mathbf{P} = \sum_{\text{over all } i \text{ conformations}} D_i \cdot \mathbf{P}_i \tag{1}$$

$$\mathbf{P}_i = \hat{\mu}\perp_i \cdot \mathrm{ROF}_\mathrm{i} \tag{2}$$

An Experimental Estimate of the Lower Limit of $\chi^{(2)}$ for Compound 1

These data prove unequivocally that the functional group orientation in the C* phase of compound **1** close to room temperature is good (much better than can be achieved by electrical poling), and that compound **1** should possess a large $\chi^{(2)}$ relative to other known FLC materials. Unfortunately, the measurement of the components of the *d* tensor for **1** by angle phase-matched SHG has proven problematical so far. This is not due to difficulty in the measurement, but rather is due to difficulty in obtaining a well homeotropically-aligned cell.

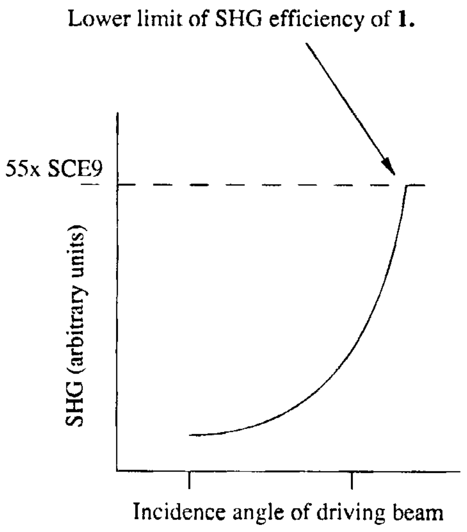
In order to get some idea of the optical nonlinearity of **1**, an SHG experiment was accomplished using a 10 μm parallel-aligned sample. In this geometry, the input IR beam must make a very acute angle with the surface of the cell, and before the phase-matched peak was reached, light input into the cell was cut off by total internal reflection at the glass-LC interface.

Nevertheless, as indicated in Figure 3, the *lower limit* of the SHG intensity from compound **1** at the phase-matched peak is 55 times that of SCE9, giving a lower limit on $\chi^{(2)}$ as measured by the d_{eff} for SHG of greater than 0.07 pm/V, and suggesting that the lower limit on the largest component of the d tensor is probably greater than 0.5 pm/V ($d_{23} \cong 7 \times d_{\mathrm{eff}}$ for SCE9). We suggest this is actually quite a conservative estimate.

CONCLUSIONS

The small table at the lower right of Figure 3 summarizes the primitive state of the art in $\chi^{(2)}$ FLCs, with values of the polarization, SHG efficiency, and d_{eff} for ZLI 3654, SCE9 and the lower limits for **1**. While questions remain concerning the actual magnitude of $\chi^{(2)}$ in thin films of compound **1**, this material shows the highest measured $\chi^{(2)}$ of any FLC to date, though the lower limits are still quite small relative to $LiNbO_3$.

The polarization measurements, however, prove that good polar orientation of functional arrays with moderate β is achievable in FLC films, and further work aimed at characterization of the compounds in Chart 1, and at synthesis of new $\chi^{(2)}$ FLC materials is in progress. Finally, we point out that generally *solids* are more desirable than liquids in typical applications of $\chi^{(2)}$ thin films. In this regard,



deff = -d14 sin(2θ) + d23 sin^2θ + d16 cos^2θ

= 0.01 pm/V for SCE9 (note this value is 7 times smaller than the largest coefficients for SCE9 = d23 = 0.073 pm/V)

deff^2 (1)/deff^2 (SCE9) > 55 at the phase matching angle.

deff (1) > 0.07 pm/V

Summary

cmpd	$\lvert P \rvert$	SHG†	d_{eff}
ZLI-3654	29	1	0.005
SCE9	33	5	0.01
1	480*	>275	>0.07

† SHG efficiency as measured by the relative intensity of the SHG signal at the top of the phase-matched peak.

* The SHG efficiency of **1** was measured at 50°C, were **P** = -480 nC/cm^2.

FIGURE 3 Preliminary results on evaluation of the second order susceptibility of **1**.

the prospects for obtaining FLC *polymer* (FLCP) films with useful $\chi^{(2)}$ seems particularly exciting. This is especially true given that we have recently obtained good evidence that the functional group orientation occurring in high polarization polysiloxane side-chain FLCPs can be similar to that occurring in the analogous low molecular weight mesogens.[23] Indeed, the synthesis of a polysiloxane side-chain FLCP possessing the mesogenic units of compound **1** has been recently achieved in our laboratories, and characterization of that material is in progress. Note that the polymer glass obtained upon cooling of an FLCP is unique, apparently possessing thermodynamically stable polar order in a non-crystalline solid material. If large $\chi^{(2)}$ could be obtained, such glasses would appear to provide an interesting solution to many second order NLO materials problems.

Acknowledgment

This work was supported in part by the Office of Naval Research. In addition, M. B. Ros would like to thank the Ministerio de Educación y Ciencia of Spain for financial support.

References

1. D. J. Williams, *Angew. Chem. Int. Ed. Engl.*, **23**, 690–703 (1984).
2. Synthesis of "single-molecule" materials is illustrated by the "molecular tinker toys" approach of Michl: K. Hassenrück, G. S Murthy, V. M. Lynch and J. Michl, *J. Org. Chem.*, **55**, 1013–1016 (1990).
3. S. R. Marder, J. W. Perry and W. P. Schaefer, *Science*, **245**, 626–628 (1989).
4. (a) T. M. Leslie, R. N. Demartino, E. W. Choe, G. Khanarian, D. Haas, G. Nelson, J. B. Stamatoff, D. E. Stuetz, C.-C. Teng and H.-N. Yoon, *Mol. Cryst. Liq. Cryst.*, **153**, 451–477 (1987); (b) C. W. Dirk and M. G. Kuzyk, *Chemistry of Materials*, **2**, 4–6 (1990); (c) A. A. Dembek, C. Kim, H. R. Allcock, R. L. S. Devine, W. H. Steier and C. W. Spangler, *Chemistry of Materials*, **2**, 97–99 (1990).
5. (a) R. Popovitz-Biro, K. Hill, E. M. Landau, M. Lahav, L. Leiserowitz and J. Sagiv, *J. Am. Chem. Soc.*, **110**, 2672–2674 (1988); (b) R. Popovitz-Biro, K. Hill, E. Shavit, D. J. Hung, M. Lahav, L. Leiserowitz, J. Sagiv, H. Hsiung, G. R. Meredith and H. Vanherzeele, *J. Am. Chem. Soc.*, **112**, 2498–2506 (1990).
6. N. Tillman, A. Ulman, J. S. Schildkraut and T. L. Penner, *J. Am. Chem. Soc.*, **110**, 6136–6144 (1988).
7. D. M. Walba, M. B. Ros, N. A. Clark, R. Shao, K. M. Johnson, M. G. Robinson, J. Y. Liu and D. Doroski, "Design of Ferroelectric Liquid Crystals for Electronic NLO Applications," in *New Materials for Nonlinear Optics*, G. D. Stucky, (Ed.); ACS Symposium Series, American Chemical Society, Washington, DC, In press.
8. J. A. Giordmaine, *Phys. Rev.*, **138**, A1599–A1606 (1965).
9. P. M. Rentzepis, J. A. Giordmaine and K. W. Wecht, *Phys. Rev. Lett.*, **16**, 792–794 (1966).
10. T. Hahn and H. Klapper, "Point Groups and Crystal Classes," in *International Tables for Crystallography*, T. Hahn, (Ed.); D. Reidel Publishing Company, Dordrecht, Holland, 1983; Vol. A, pp 745–786.
11. A. N. Vtyrin, V. P. Ermakov, B. I. Ostrovskii and V. F. Shabanov, *Sov. Phys. Crystallogr.*, **26**, 309 (1981).
12. (a) A. Taguchi, Y. Ouchi, H. Takezoe and A. Fukuda, *Jpn. J. Appl. Phys.*, **28**, L997–L999 (1989); (b) A. Taguchi, K. Kajikawa, Y. Ouchi, H. Takezoe and A. Fukuda, "Second Harmonic Generation in Ferroelectric Liquid Crystals," *Nonlinear Optics of Organic and Semiconductors*, T. Kobayashi, Editor, Springer Proceedings in Physics, Vol 36, 250–253 (1989).
13. J. Y. Liu, M. G. Robinson, K. M. Johnson and D. Doroski, *Optics Letters* **15**, 267–269 (1990).
14. D. M. Walba, S. C. Slater, W. N. Thurmes, N. A. Clark, M. A. Handschy and F. Supon, *J. Am. Chem. Soc.*, **108**, 5210–5221 (1986).
15. D. M. Walba, R. T. Vohra, N. A. Clark, M. A. Handschy, J. Xue, D. S. Parmar, S. T. Lagerwall

and K. Skarp, *J. Am. Chem. Soc.*, **108**, 7424–7425 (1986); (b) D. M. Walba and N. A. Clark, *Ferroelectrics*, **84**, 65–72 (1988); (c) D. M. Walba, H. A. Razavi, N. A. Clark and D. S. Parmar, *J. Am. Chem. Soc.*, **110**, 8686–8691 (1988).

16. K. Furukawa, K. Terashima, I. Mitsuyoshi, S. Saitoh, K. Miyazawa and T. Inukai, *Ferroelectrics*, **85**, 451–459 (1988).
17. D. M. Walba, H. A. Razavi, A. Horiuchi, K. F. Eidman, B. Otterholm, R. C. Haltiwanger, N. A. Clark, R. Shao, D. S. Parmar, M. D. Wand and R. T. Vohra, *Ferroelectrics*, In press.
18. (a) A. Dulcic and C. Sauteret, *J. Chem. Phys.*, **69**, 3453–3457 (1978); (b) C. W. Dirk, R. J. Twieg and G. Wagniére, *J. Am. Chem. Soc.*, **108**, 5387–5395 (1986); (c) D. Li, T. J. Marks and M. A. Ratner, *Chem. Phys. Lett.*, **131**, 370–375 (1986).
19. (a) J. W. Goodby, G. W. Gray and D. G. McDonnel, *Mol. Cryst. Liq. Cryst.*, **34**, 183–188 (1977); (b) J. W. Goodby and T. M. Leslie, *Mol. Cryst. Liq. Cryst.*, **110**, 175–203 (1984).
20. T. Inukai, S. Saitoh, H. Inoue, K. Miyazawa, K. Terashima and K. Furukawa, *Mol. Cryst. Liq. Cryst.*, **141**, 251 (1986).
21. P. Martinot-Lagarde, *J. Phys. Colloq. (Orsay, Fr.)*, **37**, 129 (1976).
22. In previous incarnations of the Boulder Model, a dielectric constant was included in Equation 2, which relates the magnitude of the observed ferroelectric polarization to the microscopic molecular dipoles (Reference 14). We now feel that additional terms in Equation 2 are probably unnecessary.
23. (a) D. M. Walba, P. Keller, D. S. Parmar, N. A. Clark and M. D. Wand, *J. Am. Chem. Soc.*, **111**, 8273–8274 (1989); (b) D. S. Parmar, N. A. Clark, P. Keller, D. M. Walba and M. D. Wand, *J. Phys. (Les Ulis, Fr)*, **51**, 355–368 (1990).