

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 retinoids¹ 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

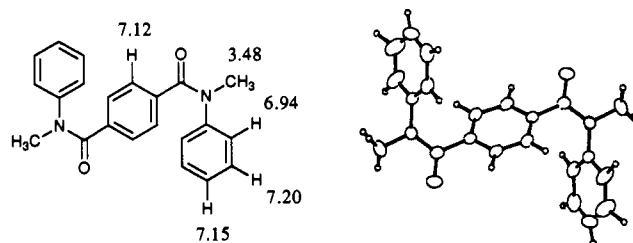


Figure 1. Structure and an ORTEP view of 3.

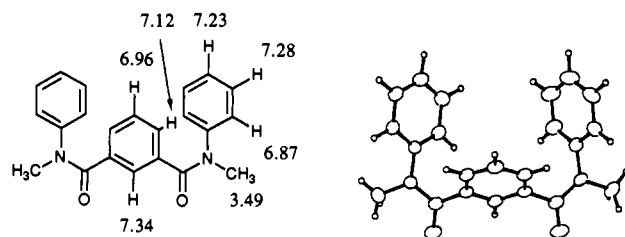


Figure 2. Structure and an ORTEP view of 4.

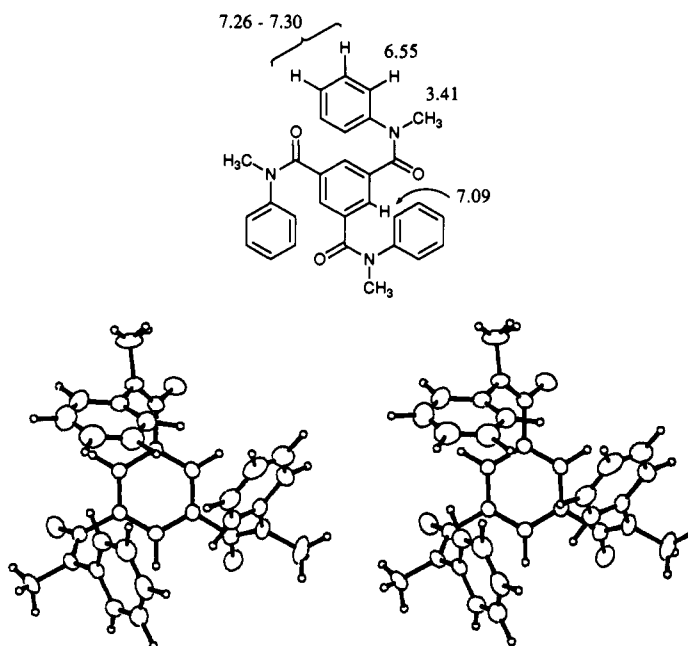


Figure 3. Structure and an ORTEP stereoview of 5.

NMR spectrum⁴ 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.

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 CDCl₃. Chemical shifts (at -60 °C) for compounds 3-5 and 7 are shown in the figures. The dynamic aspects will be discussed elsewhere.

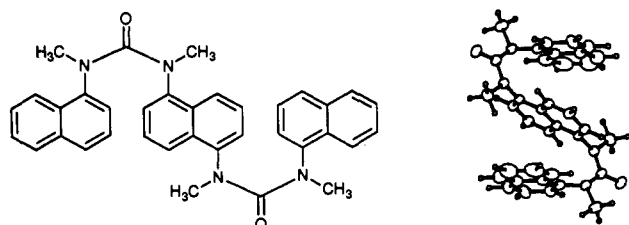


Figure 4. Structure and an ORTEP view of 6.

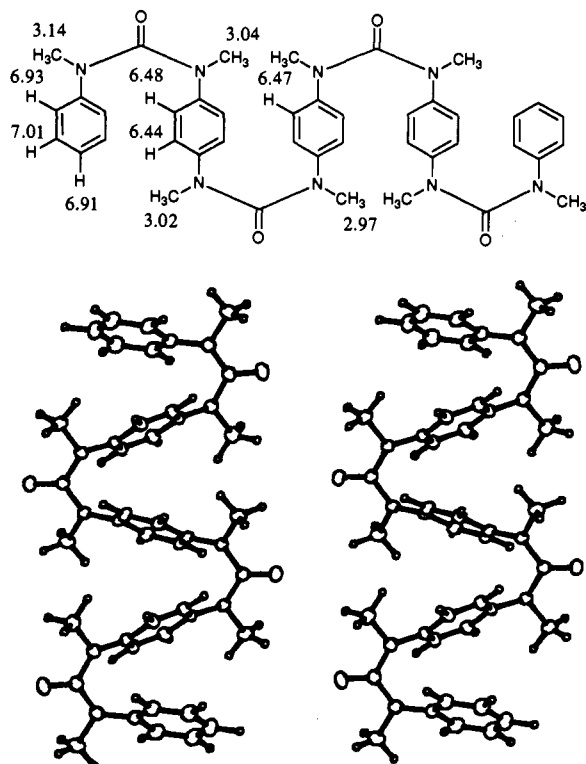


Figure 5. Structure and an ORTEP stereoview of 7.

field chemical shift of the ortho protons may reflect the combined anisotropic effects of the central benzene ring and an adjacent aniline ring.

Another interesting example of stereochemical switching was found during the N-methylation of ureas. Aromatic ureas exist in transoid structures.⁶ However, the *cis* preference of *N*-methyl-*N,N'*-diphenylureas⁷ and the *bis-cis* preference of *N,N'*-dimethyl-*N,N'*-diphenylurea⁸ also seem to be intrinsic. Two examples, *N,N',N'',N'''*-tetramethyl-1,5-bis(1-naphthylureido)-naphthalene (6) and an *N*-methyl derivative of a poly(phenyleneureido)benzene (7) may be of interest.

The *bis-cis* conformation of the ureido structure of 6 is retained in both the ureido structures (Figure 4). An NMR study on 6 was not very informative, but definitely showed the presence of at least partial aromatic-aromatic interactions. The structure of the five-layered urea derivative (7) is beautifully shown in Figure 5. The angle between the first and the second benzene-ring planes is 38.5° and that between the second and the third ring planes is 46.7°. The angle between the first and the third is 12.1°, close to parallel, and the distance between the parallel second and fourth planes is 7.29 Å. The distances between aromatic carbon atoms bearing a nitrogen atom are 3.31 Å (the first and second) and 2.96 Å (the second and third). The solution stereochemistry is

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considered to be quite similar to the crystal structure: the NMR chemical shifts presented in the structure for the terminal aromatic rings are close to those of *N,N'*-dimethyl-*N,N'*-diphenylurea,⁷ and the chemical shifts for the second and third aromatic rings are very close to those of the central ring of *N,N',N''*-trimethyl-1,4-bis(phenyleneureido)benzene, which also exists in a similar layered structure.⁸ Nuclear Overhauser effects are also consistent with the assigned solution structure. In this system, some aromatic interactions (close to parallel benzene-benzene interactions)⁵ probably exist, and such long-range aromatic-aromatic interactions may constitute a new area of chemical research.

The examples shown here are only fundamental compounds, but they demonstrate the usefulness of the *N*-methylamide moiety in constructing molecular structures of various types. The ease of introduction of the *N*-methylamide moiety into molecules makes this strategy attractive in molecular design.

Supplementary Material Available: X-ray crystallographic details for compounds 3-7 including the atom-numbering scheme and tables of bond lengths and angles, atomic coordinates, and anisotropic thermal parameters (20 pages); listing of observed and calculated structure factors for compounds 3-7 (33 pages). Ordering information is given on any current masthead page.

Fluorinated Fullerenes

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The fullerenes, C₆₀ and C₇₀, have received much attention recently.¹⁻⁴ They are now considered to be a new allotropic form of carbon. All the carbon atoms in C₆₀ are equivalent. Therefore, one might expect a fully fluorinated molecule of stoichiometry C₆₀F₆₀. Such a molecule, as well as C₆₀H₆₀, has indeed been calculated to be stable.⁵ We have undertaken the fluorination of powdered materials containing C₆₀ and C₇₀ in various ratios.

Starting materials were prepared via standard techniques: soot production by "burning" graphite rods in a 300-Torr helium atmosphere and Soxhlet extraction in boiling toluene, followed in some cases by liquid chromatography in hexanes on neutral alumina.⁶ The resulting powders were dried in flowing nitrogen at 400 °C to drive off all traces of solvent. Most experiments were carried out on unpurified extract containing about 10% C₇₀; mass spectra were also measured on a 90% C₇₀ sample.

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