“Is it possible to aggregate dipolar molecules in condensed phase in such a way that all molecular dipole moments are dipole-parallel aligned?” This dipole-parallel alignment problem presents a grand challenge. Many thought about the problem and wrote that it cannot be solved. The problem is illustrated in Scheme 1 where each arrow presents one molecule with a significant dipole moment. Collinear dipoles will align themselves parallel. The question is whether dipole-parallel alignment can be achieved in the second and third dimensions. Usually, neighboring strings of collinear dipoles will run in the opposite direction and no net dipole moment results (left in Scheme 1). We aim to create two-dimensional polar order as shown in the center of Scheme 1 and to stack the polar sheets in the third dimension again with dipole-parallel alignment. Any close approximation (such as Scheme 1, right) would present a significant advance.

Evolution has not been able to solve the dipole-parallel alignment problem in any significant way. Complexity is probably highest in protein structures and all known bundles of $\alpha$-helices are antiparallel and all close neighbors are antiparallel in all known four-helix bundles. The “best” nature has come up with are so-called $\alpha,\beta$-barrels in which parallel-dipole aligned helices are held in place by an infrastructure of $\beta$-sheets.

In the mid-1990s, we studied the energies of point dipole lattices and made an important discovery: As expected, antiparallel alignment is always preferred over the parallel-aligned lattice, but, and this insight came as paradigm-shifting surprise, the latter might be a local minimum! We examined one special path for a cooperative relaxation and this path...
Scheme 1. Strategies for the achievement of polar order must overcome the intrinsic preference for the antiparallel alignment of neighboring strings.

had a barrier (Fig. 1). This discovery placed the problem in an entirely different light and it became clear that a solution of the dipole alignment problem was not hopeless. The study also provided all the guidance we needed (Scheme 2). First, the molecular dipoles should be modest so that parallel alignment can compete with antiparallel alignment. Second, the molecules need to be designed such that additional attractive interactions stabilize the desired dipole-parallel-aligned lattice more than any possible dipole-antiparallel lattice. These ideas led to the design ideas illustrated in Scheme 2 and their realization with unsymmetrical acetophenone azines. Conjugated acceptor-donor-substituted systems were sought with little or no through-conjugation in the ground state (but the possibility for such conjugation in excited states). The placement of two acceptors with opposite polarity in the center of the molecules achieves this design goal of “dipole minimization” as one half of the molecule remains dipolar while the other half is rendered quadrupolar along the long axis. The “alignment units” are arenes. Arenes have high quadrupole moments and our design sought to employ arene–arene interactions as lateral synthons. Two alignment units will provide for two side-by-side dipolar molecules to be either parallel or antiparallel. Since the arene–arene interactions for the parallel and antiparallel side-by-side arrangement differ, it is entirely possible to bias the system such that parallel-dipole alignment becomes thermodynamically preferred.

Lateral Arene–Arene Interactions and Perfect Dipole-Parallel Alignment in Two Dimensions

The (MeO,Br)-azine, MeO–Ph–CMe=N=N=CMe–Ph–Br, was our first breakthrough5,6 and its crystal structure is shown in Figure 2. Perfect dipole-parallel alignment was achieved in two dimensions and the alignment in the third direction was near-perfect.
Figure 1. Potential energy surface along a path for the cooperative conversion of a dipole-parallel aligned crystal into a dipole-antiparallel aligned dipole lattice as $\Theta$ varies.

The dipole-parallel alignment problem really is a two-dimensional (2D) problem and we think of it as the problem of making 2D layers that contain side-by-side parallel dipoles that are more or less perpendicular to the layer surfaces. Once such polar 2D layers are constructed, they must stack in a polar fashion. One such perfectly dipole-parallel-aligned layer of the (MeO,Br)-azine is shown in Figure 3.

Each molecule A (B) interacts with two other A (B) molecules and the interactions involve two offset face-to-face arene–arene contacts of the (ff|ff) type (Fig. 4). In addition, each A engages in four contacts
Scheme 2. Chromophore design to afford ground-state dipole minimization.

Figure 2. Crystals of the (MeO,Br)-azine contain perfectly dipole-parallel-aligned layers and these layers are stacked in the b-direction.

with B molecules and all these contacts are double-T contacts\(^7,8\) of the (ef|fe) type. For interacting diarenes, the (12|34) abbreviation specifies for each arene whether it acts as a “face” or an “edge,” the (12] refers to one molecule and the [34] to the other, and it is understood that 1 interacts with 3 and 2 with 4. There are two fundamentally different and diastereoisomorphic (ef|fe) contacts, the open and closed contacts are schematically shown in Scheme 3, and they are illustrated in Figure 5. Each of these contacts occurs twice because there are two independent molecules.

In the following years, we succeeded in crystallizing the (MeO,Cl)-azine\(^9\) and the (MeO-I)-azine\(^10\) and their crystal packings are analogous with
Figure 3. One layer of the (MeO,Br)-azine viewed along the long axis of the molecules with bromine atoms close (left) and the methoxy groups close (right). Hydrogen atoms omitted for clarity. The layer contains columns of two independent molecules A and B.

Figure 4. Columns of twisted molecules A are formed with offset face-to-face arene–arene interactions of the (ffff) type.

As we searched for more aligned unsymmetrical azines, we studied the symmetrical azines (X = Y) in very much detail. We prepared and crystallized (E,E)-configured, para-disubstituted azines starting with a discussion of the (X = Y = OCOEt)-azine, followed by a communication of a
Scheme 3. Diarenes with spacers with lateral offset allow for isomeric (ef|fe) contacts, the so-called “open” and “closed” (ef|fe) contacts.

Figure 5. Double-T (ef|fe) contacts are the dominant lateral synthon. There are four such contacts between A and B; one “open” (top) and one “closed” contact are shown.
series of halogenated systems (H, F, Cl, Br, CN)\textsuperscript{12} later completed with our report of the iodo-azine,\textsuperscript{13} corroborated with a discussion of polymorphism in the para-tolyl azine,\textsuperscript{14} and completed with a comprehensive comparative analysis that also included a variety of other oxygen, nitrogen, and carbon substituents (X = Y = OMe, OH, OCOEt, NMMe\textsubscript{2}, NH\textsubscript{2}, NO\textsubscript{2}, COOEt, CN).\textsuperscript{15} Asymmetrization effects commonly are discussed on the basis of structural features of the unsymmetrical systems. Our data for the symmetrical and the unsymmetrical azines allowed for a direct comparison of structural effects of asymmetrization and the analysis showed in a compelling fashion that there are no structural manifestations of asymmetrization at all. In fact, crystal packing effects are magnitudes larger than any such electronic effects would be. Hence, we performed a theoretical gas phase study of asymmetrization effects on the structures and populations\textsuperscript{16} and an experimental solution phase NMR study\textsuperscript{17} of symmetrical and unsymmetrical azines. Both studies demonstrated that the azine bridge indeed acts as a conjugation stopper; the electronic effects of asymmetrization are negligible in the ground state. Current research focuses on comparative analyses of azines with their respective dienes.\textsuperscript{18}

**Interlayer Binding Control and Perfect Dipole-Parallel Alignment in Three Dimensions**

The explanation of the kink in the alignment of the layers in the (MeO,X)-azines required another major adjustment in common thinking. At first we thought the interlayer interaction suffered from repulsion between the halogen atoms and the proximate methoxy-O atoms. Yet, just the opposite is true! It is in fact the directionality of the attractive “halogen bonding” (dashed bonds in Fig. 6) between the haloarene and the methoxy-O atoms that causes the observed layer stacking stereochemistry. As part of a study of halogen bonding of a variety of iodo-substituted arenes, we considered the DMSO complex of the (I,I)-azine shown in Figure 7 and found a binding energy per halogen bonding contact of 5.2 kcal/mol. The binding energy computed for this structure at the MP2/LANL2DZ level is 6.4 kcal/mol. The geometries of the DMSO complexes are such that one sp\textsuperscript{2}-O-lone pair is used to form the dative bond to the halogen. Two types of halogen bonding interactions occur in the azine crystals: The geometry of the longer contact suggests the orientation of one sp\textsuperscript{3}-O-lone pair toward the halogen while the halogen is placed “between the ether lone pairs” in the shorter contact (Scheme 4).

Replacement of the methoxy by a decoxy group should disrupt any halogen bonding and avoid directional preferences in the interlayer adhesion. Since the layer as a whole has a strong macroscopic dipole moment, and in the absence of other effects, the stacking should lead preferentially to dipole-parallel alignment. Indeed, the crystal structure of the (DecO,Br)-azine is perfectly dipole-parallel aligned (Fig. 8).

**Perspective**

We have accomplished perfect dipole-parallel alignment in crystals of polar organic molecular materials. The perfect alignment is achieved without electric field alignment and, hence, the materials show no relaxation...
Figure 6. Halogen bonding (dashed bonds) between the layers provides directionality to interlayer bonding in the crystal structure of the (MeO,Br)-azine.

Figure 7. Halogen bonding in the B3LYP/LANL2DZ optimized complex between the (I,I)-azine and two molecules of DMSO.

Scheme 4. The term “halogen bonding” refers to an attractive donor-acceptor interaction in which a halogen atom serves as Lewis acid and a heteroatom (e.g., O, N) serves as Lewis base.
problems. The accomplishment is the result of rational design and positive and negative feedback obtained from the deep analysis of the prototypes as well as from the rigorous testing of the assumptions underlying the design. With our knowledge base growing and our understanding evolving, our success rate in making new polar crystals has accelerated tremendously. Instead of a new polar crystal every few years, we are now making a few perfectly polar crystals per year. In the future, we will be increasingly interested in making materials that are polar and feature additional desirable properties.

With these series of highly anisotropic and polar crystalline materials available, we now have created the unique opportunity to study the effects of static polar environments on molecular properties in a systematic fashion. These studies will be fundamental and, as with all truly new avenues of research, they can be expected to lead to new materials with new properties.

We have come to like working on complex systems even though this requires a new mind set and a break with what some have called scientific intuition. In fact, scientific intuition is largely based on very simple systems and the properties of simple systems often discourage one from taking a certain direction. Complexity introduces new options (e.g., the barrier in Fig. 1) and scientific success will rely less on reductionism and instead will emanate from the recognition of the new options presented by complexity.

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